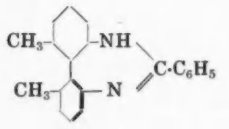
THE FORMATION OF CYCLIC COMPOUNDS FROM DERIVATIVES OF DIPHENYL. PART II.[1] THE FORMATION OF 4, 5, 9, 10-DIBENZOPYRENE AND 4, 5-DIPHENYLDIPHENYLENE OXIDE FROM 6, 6′-DIPHENYLDIPHENYL-2, 2′-TERAZONIUM SULPHATE.

See errata V.9, P. 052

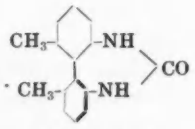
By Shin-ichi SAKO.

Received November 20th, 1933. Published February 28th, 1934.

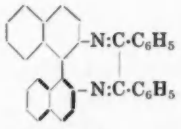
It has been found that 7- or 8-membered rings formed through the 2, 2′-positions of diphenyl compounds assume nonplanar unstrained configurations. This was demonstrated by the fact that when 7- or 8-membered rings were formed through the 2, 2′-positions of certain optically active 2, 2′, 6, 6′-substituted diphenyls the products still retained optical activity. Thus, the compounds (I), (II) and (III) produced respectively from *l*-2, 2′-dimethyl-6, 6′-diaminodiphenyl[1] and *d*-2, 2′-diamino-1, 1′-dinaphthyl[2] were optically active.



(active)
(I)

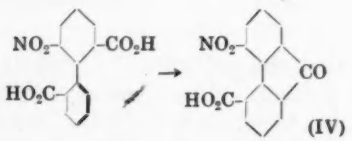


(active)
(II)

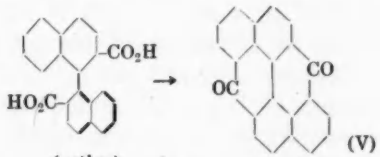


(active)
(III)

On the other hand, it has been shown by a number of examples that the products obtained by the closure of 5- and 6-membered rings through the 2, 2′-positions of optically active diphenyl compounds are optically inactive. *d*-2-Nitro-6,6′-dicarboxydiphenyl and *d*-2,2′-dicarboxy-1,1′-dinaphthyl, on heating with sulphuric acid, gave respectively the inactive compounds (IV) and (V).[3]



(active) (inactive) (IV)

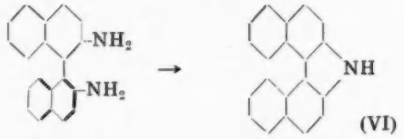


(active) (inactive) (V)

(1) For previous paper see Sako, *Mem. Coll. Eng. Kyushu Imp., Univ.*, **6** (1932), 263.
(2) Kuhn and Goldfinger, *Ann.*, **470** (1929), 183.
(3) Bell and Robinson, *J. Chem. Soc.*, **1927**, 2238; Kuhn and Albrecht, *Ann.*, **465** (1928), 282.

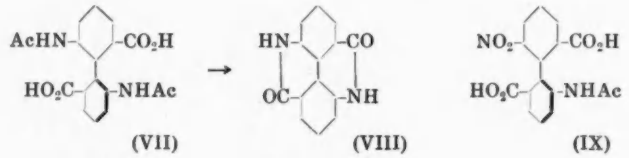
CHEMISTRY LIBRARY

Similarly, inactive naphthocarbazol (VI) was obtained by heating either the *d*- or *l*-form of 2, 2′-diamino-1, 1′-dinaphthyl with hydrochloric acid.[2]



(active) (VI) (inactive)

when *l*-6, 6′-diacetamidodiphenic acid (VII) was hydrolysed by cold sulphuric acid an inactive dilactam (VIII) was produced.[4]



(VII) (VIII) (IX)

(active) (inactive)

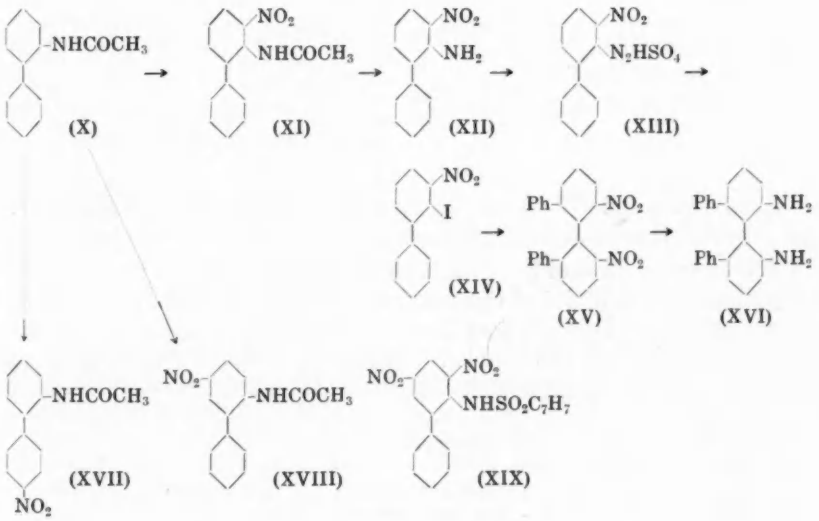
Since most of these active substances are stable toward heat or toward chemical reagent, the disappearance of optical activity is supposed to be due, not to racemization, but to the change from a spatial arrangement to a coplanar structure. But in view of the fact that the formation of all but one of the 5- or 6-membered rings in the above examples was effected by heating and also that such a compound as (VII), the only substance from which ring formation was accomplished in the cold, does not appear to be a suitable substance, for it has been found that the active forms of the compound (IX) which is a somewhat similar substance to (VII) in constitution easily racemizes in hydrochloric acid solution even at ice-cold temperatures (the unpublished result of the author.), it may be stated that the evidence furnished by these examples is not as conclusive as is desirable for demonstrating the correctness of this supposition.

Meisenheimer and Höring[4] stated that the sodium salt of the active substance (VII) is stable toward heat but this can not be taken as indicating the stability of the free acid, for the author found that the active form of (IX), though not stable as free acid, was stable in the form of its sodium or ammonium salt in similar circumstances. In order to place this supposition on a firmer ground it is desirable to use an active substance which is not

(4) Meisenheimer and Höring, *Ber.*, **60** (1927), 1433.

only quite resistant to racemization but also produces 5- or 6-membered rings through the 2, 2′-positions with ease at as low a temperature as possible. The substance which adequately fulfils these conditions seemed to be 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI) in which the presence of the phenyl groups would perhaps stabilize the optical isomers. It is to be expected also that the tetrazonium salt prepared from (XVI), judging from its constitution, might decompose in three ways resulting in the formation of either two 6-membered rings or one 5-membered ring through the 2, 2′-positions or of two hydroxyl groups in the 2, 2′-positions. Although the intended object was not attained on account of the fact that attempts to separate 2, 2′-diamino-6, 6′-diphenyl diphenyl into optical antipodes have not so far been unsuccessful, a description of the preparation of this compound (XVI) and the decomposition products of the tetrazonium salt derived therefrom may be of use.

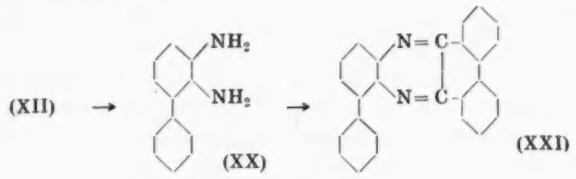
The starting substance for the preparation of 2, 2′-diamino-6, 6′-diphenyl diphenyl was 2-acetamidodiphenyl (X) which on nitration with a specially devised method yielded 3-nitro-2-acetamidodiphenyl (XI). This could be successively converted into 2-amino-3-nitrodiphenyl (XII), its diazonium sulphate (XIII) and 3-nitro-2-iododiphenyl (XIV), and the latter treated according to the Ullmann method with copper powder. 2, 2′-Dinitro-6, 6′-diphenyl diphenyl (XV) produced in this way on reduction gave 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI):



Two mononitro derivatives of 2-acetamidodiphenyl have been recorded in the literature: one of these, 4′-nitro-2-acetamidodiphenyl (XVII) was obtained as the primary product by acting nitric acid on 2-acetamidodiphenyl in a mixture of sulphuric acid and acetic acid,[5] while the other, 5-nitro-2-acetamidodiphenyl (XVIII) was obtained in the presence of acetic acid alone.[6] The only substance recorded, having a nitro-group in the ortho-position to the amino-group, was a dinitro-compound, 3, 5-dinitro-2*p*-toluene sulphonamidodiphenyl (XIX).[6]

Applying the method of Witt and Utermann[7] for the preparation of *o*-nitroaniline which consisted in nitrating the acetanilide in a mixture of acetic anhydride and acetic acid it was found that 3-nitro-2-acetamidodiphenyl could be obtained as one of the two products, the other product being 5-nitro-2-acetamidodiphenyl (XVIII). The Witt and Utermann method thus seems capable of general application for the preparation of similar derivatives of *o*-nitroaniline, for 3-nitro-*o*-toluidine proved also to be obtainable in a good yield from *o*-acetotoluidide by the same method.[8]

The constitution of the 3- and 5-nitro-2-aminodiphenyl thus obtained were confirmed by the examination of their reduction products, the diamino-compounds. 2, 3-Diaminodiphenyl (XX) obtained from (XII) on treatment with hydrochloric acid and ferric chloride gave the deep red diaminophenazine derivative and with phenanthrene quinone the 2, 3-(*oo*′-diphenylene)-5-phenyl quinoxaline (XXI):



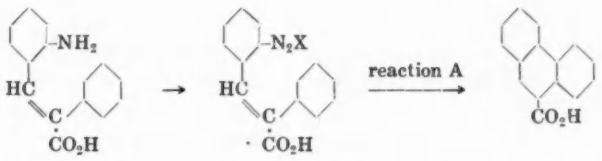
Similarly, 2-amino-5-nitrodiphenyl was converted into 2, 5-diaminodiphenyl which showed characteristic reactions of *p*-phenylene diamine.

Although the yield of 3-nitro 2-acetamidodiphenyl (XI) from 2-acetamidodiphenyl was but 22.6% of the theoretical, thanks to the fact that, in the subsequent stages of preparations, 3-nitro-2-iododiphenyl (XIV), 2, 2′-dinitro-6, 6′-diphenyl diphenyl (XV), and 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI) were under favourable conditions all produced in the almost quantitative

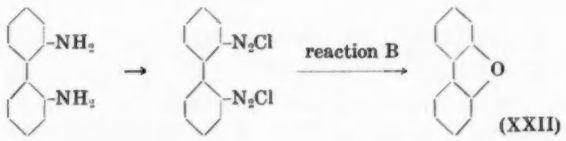
(5) Scarborough and Waters, *J. Chem. Soc.*, **1927**, 89.
(6) Bell, *J. Chem. Soc.*, **1928**, 2773.
(7) *Ber.*, **39** (1906), 3061; **41** (1908), 3090 Anm.
(8) Gabriel and Thieme, *Ber.*, **52** (1919), 1080.

yield, this work was made possible to proceed to further stages. At first, the problem of diazotizing 2-amino-3-nitrodiphenyl (XII) which had difficultly salt-forming property seemed a difficult one, but this could be surmounted by the use of conc. sulphuric acid in which the compound was diazotized smoothly.

It has already been stated that the tetrazonium salt derived from 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI) might decompose in three different ways. In the first place it will be remembered that there exists among compounds containing two benzene rings between which two carbon atoms are present and having in the ortho-position of one of the benzene rings a diazonium salt group a marked tendency with the loss of nitrogen to form a 6-membered ring resulting in the direct linking of the benzene rings. As an example for this may be cited the well-known synthesis of phenanthrene carboxylic acid by Pschorr's method[9] from *α*-phenyl *o*-aminocinnamic acid (reaction A):



These conditions are as a matter of fact present on either side of the molecule of the tetrazonium salt obtainable from 2, 2′-diamino-6, 6′-diphenyl diphenyl (XVI). On the other hand, it will be recalled that when tetrazonium chloride solution prepared from 2, 2′-diaminodiphenyl, of which (XVI) is a derivative, was heated[10] diphenylene oxide (XXII) was produced in a 70 per cent. yield (reaction B):



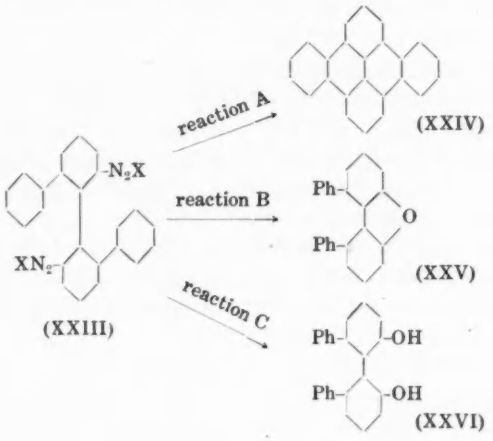
(XXII)

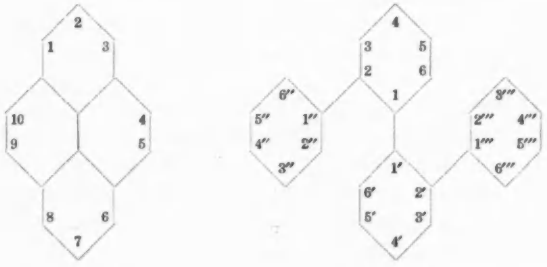
Finally, another possible decomposition of the tetrazonium salt is the production of the dihydroxyl compound without ring formation (reaction C). Thus in the decomposition of the tetrazonium salt (XXIII) obtained from 2, 2′-diamino-6, 6′-diphenyl diphenyl, according to whether reaction A,

(9) *Ber.*, **29** (1896), 496.

(10) Täuber and Halberstadt, *Ber.*, **25** (1892), 2745.

reaction B or reaction C occurs 4, 5, 9, 10-dibenzopyrene (XXIV),[11] 4, 5-diphenyl diphenylene oxide (XXV), or 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl (XXVI) would result:





It would be reasonably supposed that the general principles stated in those views on the ease of formation of carbon rings[12] can be applied equally to the formation of rings other than saturated. And if so, it may be stated at once that in the decomposition of the tetrazonium salt (XXIII) reaction A should take place more easily than reaction B, since, if the accepted formula for diphenyl is correct, the condition under which 4, 5, 9, 10-dibenzopyrene (XXIV) is to be formed is perhaps one of the most favourable one

(11) The numbering for pyrene (XXVII) is one that was described in C., *Gen. Reg.*, VI (1922–1924), T. II, 816, for naming the then only known dibenzopyrene, 1, 2, 7, 8,-dibenzopyrene, obtained by Scholl and Neumann (*Ber.*, **55** (1922), 123), who originally adopted another mode of numbering for pyrene.

(12) Sako, this Bulletin, **9** (1934), 41.

which can be imagined in ring formation; in (XXVIII)[13] the carbon atoms 6 and 2''' (or 6''') and 6' and 2'' (or 6'') can not but come close together when the four benzene nuclei are rotated around each common axis (Normally in the central diphenyl system which has two diazonium salt groups in the 6, 6'-positions only the semi-circular rotation is possible), and moreover no strain would be produced by the ring formation, a fact which imply that 4, 5, 9, 10-dibenzopyrene should be a stable substance as it is the case with pyrene, having the carbon atoms in one plane. In reaction B however there are at least two conditions which would be unfavourable to the production of the 5-membered ring in (XXV): one, the more important of the two, is the presence of the two phenyl groups in the 2, 2'-positions which should hinder the two diazonium salt groups in the 6, 6'-positions to approach each other and the other is the production of strain which has to be overcome in forming the 5-membered ring. As a matter of fact, this inference was fully borne out by the experiment.

It has been found that, although 4, 5, 9, 10-dibenzopyrene (XXIV) is produced by the decomposition of the tetrazonium salt (XXIII) even at ice-cold temperatures, 4, 5-diphenyl diphenylene oxide (XXV) can be obtained only when the decomposition is carried out at high temperatures. And whereas the yield of the dibenzopyrene (XXIV) is almost unchanged (36–40% of the theor.) whether the tetrazonium salt (XXIII) is decomposed in the cold or by heating, the yield of 4, 5-diphenyl diphenylene oxide (XXV) shows an increase with the rise of temperature at which the decomposition is effected (null below 45°C., 12 per cent. of the theor. at 60–70°C. and 30 per cent. at 100°C.).

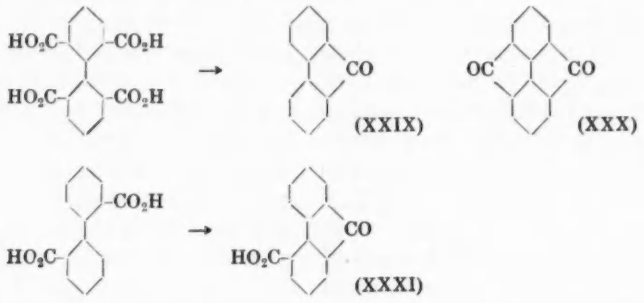
It is remarkable that neither the decomposition of the tetrazonium salt (XXIII) is at all promoted nor the yield of the dibenzopyrene (XXIV) is increased by the addition of copper powder to (XXIII), a phenomenon which is quite distinct from the production of phenanthrene carboxylic acid by Pschorr's method. As expected, 4, 5, 9, 10-dibenzopyrene is a very stable substance which melts without decomposition at 353–355°C. and can be distilled under reduced pressure.

The remarkable facility with which two six-membered rings in the dibenzopyrene (XXIV) are produced is in contrast with the repeated failure in attempting to produce two 5-membered rings, one on either side of the diphenyl molecule. Thus, fluorenone (XXIX) is produced in place of the substance (XXX) when diphenyl-2, 2', 6, 6'-tetracarboxylic acid is distilled,[14]

(13) For the ring system of 2, 2'-diphenyl diphenyl, the numbering shown by (XXVIII) is proposed.

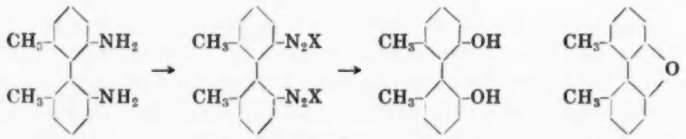
(14) Meyer, Meyer and Taeyer, *Ber.*, **53** (1920), 2034.

and the action of dehydrating agents on diphenic acid does not proceed beyond the stage of fluorenone carboxylic acid (XXXI):



This is probably due to the fact that by the formation of the 5-membered ring which may approximately be represented by a regular pentagon the distance between the carbon atoms in the 4, 5-positions is increased so that the production of the other 5-membered ring is impossible. At the same time it suggests that the fluorenone molecule has probably a coplanar structure, since if it is possible to incline the plane of the benzene rings toward each other as in the manner of the Kaufler formula for diphenyl two five-membered rings should be formed without difficulty.

The view stated above that the non-production of the diphenyl diphenylene oxide (XXV) at low temperatures is due to the blocking effect of the two phenyl groups is supported by the fact that (1) diphenylene oxide (XXII) is produced by the decomposition of the tetrazonium salt obtained from 2, 2′-diaminodiphenyl in which no such blocking group is present in nearly as good a yield at ordinary temperature (60% of the theor.) as at a high temperature (70%) and (2) the tetrazonium salt (XXXIII) derived from 2, 2′-dimethyl-6, 6′-diaminodiphenyl (XXXII) in which the methyl groups are the blocking groups on decomposition even with heating yields solely 2, 2′-dimethyl-6, 6′-dihydroxydiphenyl (XXXIV):



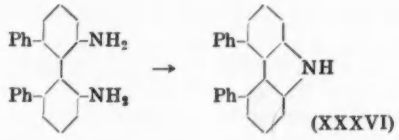
(XXXII) (XXXIII) (XXXIV) (XXXV)

In the decomposition of the tetrazonium salt (XXXIII) reaction C apparently predominates over reaction B, no trace of the diphenylene oxide

derivative (XXXV) being produced even when the decomposition is effected by heating at 100°C. This is remarkable in view of the fact that, as already stated, 4, 5-diphenyl diphenylene oxide (XXV) can be obtained in a 30 per cent. yield by heating the tetrazonium salt (XXIII) at the same temperature. This difference in behaviour between the two tetrazonium salts may be attributable to the fact that the tetrazonium salt (XXXIII) is very much less stable than (XXIII),[15] since it is possible that when heating the cold solution of (XXXIII) its decomposition is completed before ever the temperature is reached which is necessary to enforce the production of the 5-membered ring against the blocking effect of the methyl groups. As a support for this view may be adduced the fact that, as already stated, whilst the yield of diphenylene oxide (XXII) from the tetrazotized solution of 2, 2′-diaminodiphenyl in which no blocking group is present is not much influenced by the temperature at which the decomposition is effected, 4, 5-diphenyl diphenylene oxide (XXV) is produced from the tetrazonium salt (XXIII) only at high temperatures, its yield being increased with the rise of temperature.

It has been found that reaction C occurs to a very slight extent when the tetrazonium salt (XXIII) is decomposed at 100°C., the 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl (XXVI) being obtained in about 5% of the theoretical. No trace of the latter (XXVI) could be detected in the product obtained by decomposing (XXIII) at lower temperatures. In the decomposition of the tetrazotized solution of 2, 2′-diaminodiphenyl either in the cold or by heating reaction C does not occur at all, the product being solely diphenylene oxide (XXII) resulting from reaction B. The difference between the two cases may again be regarded as evidence demonstrating that the closure of the diphenylene oxide ring through the 2, 2′-positions is hindered by the blocking effect of the large groups in the 6, 6′-positions.

4, 5-Diphenyl carbazol (XXXVI), the constitution of which is analogous to 4, 5-diphenyl diphenylene oxide, has been obtained by heating 2, 2′-diamino-6, 6′-diphenyl diphenyl with hydrochloric acid:

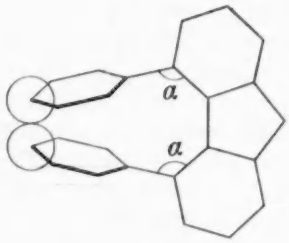


(XXXVI)

The constitution of 4, 5-diphenyl diphenylene oxide or 4, 5-diphenyl carbazol is a singular one, for if it is assumed that the diphenylene oxide

(15) The decomposition of (XXXIII) is complete in two to three days at ordinary temperature, while (XXIII) requires about a month to complete the decomposition under similar conditions.

and carbazol molecule each has a uniplanar configuration which can be roughly represented by a regular pentagon bearing regular hexagons on two of its sides, then as is clear from the diagram (XXXVII), the phenyl groups can not occupy their normal positions. In this diagram (XXXVII), the atoms constituting the carbazol or the diphenylene oxide molecule proper are supposed to be lying in the plane of the paper. The most probable form which the molecules of the substances may assume, that is to say, the least strained spatial arrangement for the valencies carrying the phenyl groups would be one in which the phenyl residues lie in planes perpendicular to the plane in which the carbazol or diphenylene oxide molecule proper lies. This is illustrated in the diagram (XXXVII) in which the heavily printed lines indicate the sides of hexagons which are nearer to the reader. If it is assumed, as shown in (XXXVII), that the relative position of the phenyl groups are to be altered only by the deflection of the angle α and that the p- and p'-carbon atoms of the phenyl groups are in contact with each other with the distance of 1.45 Å between the centres of the atoms, the angle α will be 125.1°, but as the p- and p'-carbon atoms are not in actual combination, actually the distance from the centre to centre of the carbon atoms will be somewhat longer and consequently the angle α will be somewhat larger than this. At any rate, whatever arrangement the molecule may assume, it is certain that the phenyl groups can not rotate about the bonds in these circumstances.



(XXXVII)

Experimental.

(A) *Preparation and Nitration of 2-Acetamidodiphenyl.*

2-Aminodiphenyl. The preparation of 2-aminodiphenyl from 2-nitrodiphenyl has been described by Scarborough and Waters.[15] In the following is described a method improved by the author by which this substance can be easily obtained in the theoretical yield.

To a solution prepared by passing dry hydrogen chloride into a mixture of $SnCl_2 \cdot 2H_2O$ (880 gr.) and EtOH (1000 c.c.) was added drop by drop 2-nitrodiphenyl (200 gr.) obtained by the method of Bell, Kenyon and Robinson[16]

(16) *J. Chem. Soc.*, **1926**, 1242.

in the course of one hour, HCl being led in all the time (The nitro-compound must not be added too rapidly, otherwise a violent reaction would ensue, which may be beyond control). Shortly after the addition of the nitrodiphenyl the double chloride commenced to separate as needles which was collected on the following day. The crystals thus obtained contained about 60 per cent. of the theoretical amount of 2-aminodiphenyl, the rest, 40%, being obtained from the filtrate. The crystals was then dissolved in water, treated with alkali and the base thus set free extracted with ether. The ethereal residue, on distillation under diminished pressure gave pure 2-aminodiphenyl which had b.p. 135°C./5.5 mm. The filtrate from the double salt was concentrated in a basin on the water bath into half the original bulk, made alkaline, and the base thus separated purified as before.

2-Acetamidodiphenyl (X). For the acetylation of 2-aminodiphenyl Scarborough and Waters[15] preferred acetyl chloride to acetic anhydride, the reason for this being, according to their statement, that the oily product obtained by heating the base with acetic acid or a mixture of acetic acid and acetic anhydride crystallized only with difficulty and with considerable loss. The author found however that the apparently poor yield of 2-acetamidodiphenyl when acetic anhydride was used was due to its extremely soluble property in acetic acid. The theoretical yield of the acetamidodiphenyl could therefore be obtained when the acid was removed. This was not the only instance observed by the author that such was the case. On more than one occasion it was found that the difficulty of crystallizing the products obtained by acetylating certain amines with acetic anhydride was due to the same cause.

Acetic anhydride (110 gr.) was added to a solution of 2-aminodiphenyl (176 gr.) in benzene (200 c.c.) at ordinary temperature. The reaction occurred at once, but it was allowed to stand until the next day to complete the separation of the crystals. 2-Acetamidodiphenyl thus obtained, 92 gr., formed needles melting at 120°C. The mother liquor containing the major part of the product was greatly diluted with benzene, shaken with a sodium carbonate solution and the benzene layer greatly concentrated. In this way 2-acetamidodiphenyl was obtained in the theoretical yield.

3-Nitro-2-acetamidodiphenyl (XI). As stated in the introduction 3- and 5-nitro-2-acetamidodiphenyl were produced by the mononitration of 2-acetamidodiphenyl in presence of acetic anhydride and acetic acid. As however the yield of the 3-nitro-compound was not good, the nitration was carried out under a great variety of conditions, but even under the best conditions thus arrived at the combined yield of the two nitration products amounted to only 50 per cent. of the theoretical, the rest being an uncrystal-

lizable syrup and tarry matter. It will be noticed in the experiment described below that the quantities of both nitric acid and acetic anhydride employed are about one and a half time the theoretical amount required for the mononitration, the reason for this being that when the theoretical quantities of these substances were used, 25 per cent. of the original compound remained unattacked. The use of more than the amount given in the direction led however to a lower yield of the desired substance.

2-Acetamidodiphenyl (42.2 gr.) was dissolved with heating in a mixture of acetic anhydride (30 c.c.) and glacial acetic acid (35 c.c.). The solution was agitated mechanically and cooled with water which was kept at about 22°C.

When the temperature of the liquid reached 23–24°C., the solution from which some crystals reappeared was treated with a solution of fuming nitric acid (20 gr.; D = 1.5) in glacial acetic acid (15 c.c.) in the manner described below. Two-fifths of the nitrating mixture was added during 20 minutes, when the reaction set in with a rise of temperature, the crystals gradually disappearing. After this stage was reached, the nitration mixture must be added more slowly so that the reaction mixture, which as stated above was cooled with water at 22°C., was maintained below 26.5°C. It should be added here that the nitration does not proceed at all should the temperature of the liquid fall below 20°C. Under the conditions described above, about 100 minutes were required for the addition of the nitrating mixture. After three additional hours' agitation, it was allowed to stand over night in an ice box. It was then poured on 600 gr. of ice water, shaken with 300 c.c. of benzene and the upper layer left in an ice box for some hours to complete the separation of 3-nitro-2-acetamidodiphenyl. The light-yellow needles were then collected and washed once with benzene. 3-Nitro-2-acetamidodiphenyl thus obtained, 9 gr., was practically pure. From the mother liquor which was shaken with a sodium carbonate solution and then concentrated into a small bulk, was obtained a further crop of the same crystals which, on crystallization once from benzene, gave 2.6 gr. of 3-nitro-2-acetamidodiphenyl which had the same purity as the main portion. The total yield of the 3-nitro-compound was therefore 11.6 gr. or 22.6% of the theoretical. It may be recrystallized easily from benzene, from which it separated as light-yellow needles melting at 188–188.5°C. (Found: N = 11.2. $C_{14}H_{12}O_3N_2$ requires N = 10.9%). Twenty c.c. of boiling benzene dissolve about 1 gr. of 3-nitro-2-acetamidodipheyl.

The combined mother liquors separated from 3-nitro-2-acetamidodiphenyl, containing 5-nitro-2-acetamidodiphenyl produced simultaneously by the nitration, were used for the isolation of the latter substance as described below.

2-Amino-5-nitrodiphenyl. As stated in the introduction, this compound has been obtained by Bell.[6] It was found that 5-nitro-2-acetamidodiphenyl contained in the filtrate separated from 3-nitro-2-acetamidodiphenyl did not crystallize even when the filtrate was greatly concentrated. The solvent was therefore removed and the dark residual gum was purified by distillation under reduced pressure. At first some decomposition was noticeable but it ceased after a time.

The first fraction, 2.0 gr., distilled below 200°C./6 mm., the main fraction, 29.3 gr., boiling at about 245°C./6 mm. The main fraction, being also an uncrystallizable syrup, was hydrolyzed by boiling under reflux with 20 per cent. hydrochloric acid solution (90 c.c.) in an oil bath for 3 hours. The oily product was extracted with benzene and the solution, after being washed with an alkaline solution, evaporated off. The residual syrup thus obtained, on distillation under diminished pressure, yielded a distillate, 21.3 gr., which for the most part had b.p. 220–225°C./6 mm. On crystallization of the distillate from ethyl alcohol (25 c.c.), 2-amino-5-nitrodiphenyl, 10.2 gr., separated in an almost pure condition. The mother liquor was once more evaporated into dryness and the residue divided by vacuum distillation into two fractions boiling below and above 200°C./6 mm. From the higher fraction was obtained by crystallization from ethyl alcohol 1 gr. of 2-amino-5-nitrodiphenyl, making the total yield to 25.7 per cent. of the theoretical. The pure 2-amino-5-nitrodiphenyl had m.p. 125°C. (Found: C = 67.0; H = 5.2; N = 13.1. $C_{12}H_{10}O_2N_2$ requires C = 67.3; H = 4.7; N = 13.1%).

On reduction this compound yielded the diamino-derivative which showed the characteristic reactions of *p*-phenylene diamine, a fact which prove the constitution of the parent substance.

2, 5-Diaminodiphenyl Dihydrochloride. A well-ground mixture of 2-amino-5-nitrodiphenyl (3.2 gr.) and $SnCl_2 \cdot 2H_2O$ (13.2 gr.) was treated with conc. HCl (25 c.c.). No change was observed at ordinary temperature, but on gentle heating the reaction started, which then proceeded to completion without further heating, the double chloride separating while still hot. After cooling, the crystals, 7.2 gr. were collected and the tin removed in the usual way. The filtrate from the tin sulphide was greatly concentrated and left to crystallize. 2, 5-Diaminodiphenyl dihydrochloride, 2.8 gr., was thus obtained as almost colourless plates. It was found that, during the concentration of the solution mentioned above, the solution was kept almost colourless and that, even if it became coloured, it could be restored colourless by passing hydrogen sulphide. For purification, the hydrochloride was dissolved in a small quantity of water and the solution thus obtained treated

with conc. HCl. The colourless plates thus precipitated were dried over soda lime (Found: HCl = 28.5. $C_{12}H_{12}N_2 \cdot 2HCl$ requires HCl = 28.4%). That the amino-groups in this substance are in the 2, 5-positions was proved by the fact that a solution of the hydrochloride, on treatment with H_2S and then with $FeCl_3$ solution, gave a deep violet precipitate.

2-Amino-3-nitrodiphenyl (XII). A hot solution of 3-nitro-2-acetamidodiphenyl (13 gr.) in ethyl alcohol (240 c.c.) was treated with conc. HCl (60 c.c.) and heated under reflux on the water bath for 5 hours. The greater part of alcohol was then removed by heating without reflux and water added. The oil thus separated was extracted with ether and the ethereal residue distilled under reduced pressure. The reddish oil thus obtained, 9.5 gr., boiling at 194–196°C./6 mm., became crystalline after a time. It melted at 44–45°C. The real m.p. might have been somewhat higher than this, but as no suitable solvent was found from which it could be crystallized, the matter was not further pursued. The analysis of the distillate gave the following result: Found, C = 67.7; H = 5.3. $C_{12}H_{10}O_2N_2$ requires C = 67.3; H = 4.4%.

2, 3-Diaminodiphenyl Dihydrochloride. A well-ground mixture of 2-amino-3-nitrodiphenyl (2 gr.) and $SnCl_2 \cdot 2H_2O$ (8 gr.) was heated with conc. HCl (25 c.c.) on the water bath for some hours until the disappearance of the original substance. After allowing to stand for the night, the double salt was filtered off and dried over soda lime in a vacuum. It was then dissolved in water, treated with H_2S and the clear filtrate concentrated until its bulk was 7–8 c.c. On addition of conc. HCl (15 c.c.), the hydrochloride of the diamino-compound separated quickly in somewhat brown needles. For purification, its solution was treated with animal charcoal and the substance reprecipitated by conc. HCl.

Like most of the orthodiamines the substance was not stable, the chlorine determination of the hydrochloride giving a figure much lower than that required by theory. But the properties and the behaviour of the substance left no doubt whatever as to its being an ortho-diamine. Thus, an aqueous solution of the hydrochloride, on treatment with ferric chloride, yielded the red precipitate of the diaminophenazine derivative, a reaction which is characteristic of orthodiamines. Further, the most convincing evidence was afforded by the formation of the quinoxaline compound by the action of phenanthrene quinone on the hydrochloride as described below.

2, 3-(oo'-Diphenylene)-5-phenyl Quinoxaline (XXI). Crystalline potassium acetate (0.6 gr.) was added to a warm solution of 2, 3-diaminodi-

phenyl hydrochloride (0.77 gr.) in ethyl alcohol (10 c.c.). After cooling, the precipitated potassium chloride was filtered off and the filtrate added to a boiling solution of phenanthrene quinone (0.55 gr.) in glacial acetic acid (100 c.c.), when the quinoxaline derivative separated in yellow needles. Heating was continued for an hour and the crystal was collected after cooling. It melted sharply at 221°C. (Found: N = 8.1. $C_{26}H_{16}N_2$ requires N = 7.9%). The yield was 0.9 gr. or 95.6 per cent. of the theoretical, calculated on the phenanthrene quinone employed.

(B) *Preparation of 2, 2′-Diamino-6, 6′-diphenyl Diphenyl and its Converison into 4, 5-Diphenyl Carbazol.*

3-Nitro-2-iododiphenyl (XIV). A suspension of 2-amino-3-nitrodiphenyl (21.4 gr.) in conc. H_2SO_4 (100 c.c.) was agitated at ordinary temperature for about one hour, that is, until a clear solution was obtained. It was then cooled with ice water and treated with ice (50 gr.) and solid sodium nitrite (7.5 gr.) with vigorous stirring which was continued for one hour. Twenty grams of ice were then added and agitation continued for 40 minutes. The addition of a further quantity (20 gr.) of ice was followed after a short time by the production of a thick foam. When this foam disappeared, a large quantity of ice was added and the solution filtered to remove a trace of insoluble matter and then treated with a solution of potassium iodide (20 gr.). A vigorous decomposition occurred, the iodo-compound separating as an oil which at once crystallized. The crude compound, 32.5 gr., was dissolved in ether, shaken with a potassium hydroxide solution, and the ether removed. The ethereal residue on distillation in a vacuum gave the 3-nitro-2-iododiphenyl (30 gr.) in a state of purity. It had b.p. 178°C/4 mm. Recrystallized from ethyl alcohol it formed yellow needles which melted at 90–91°C. (Found: I = 38.73. $C_{12}H_8O_2NI$ requires I = 39.05%).

2, 2′-Dinitro-6, 6′-diphenyl Diphenyl (XV). The copper powder (20 gr.) prepared by the method of Piccard and Larsen[17] was added within 7 minutes with vigorous agitation to 3-nitro-2-iododiphenyl (26 gr.) which was heated in an oil bath at 210-215°C, the heating being continued for 5 additional minutes. The mixture was extracted with benzene and the solution treated with animal charcoal. The crystalline residue from the benzene solution, 15.7 gr., was dissolved in boiling alcohol (800 c.c.) and the solution concentrated until half the original bulk. 2, 2′-Dinitro-6, 6′-diphenyl diphenyl separated on cooling as light-yellow crystals, 15 gr., melting at 201–

(17) *J. Am. Chem. Soc.*, **39** (1917), 2007.

202°C. The m.p. did not change with further crystallization (Found: N = 7.42. $C_{24}H_{16}O_4N_2$ requires N = 7.10%).

2, 2′-Diamino-6, 6′-diphenyl Diphenyl (XVI). A suspension of powdered 2, 2′-dinitro-6, 6′-diphenyl diphenyl (10 gr.) in a solution prepared by passing dry HCl to a mixture of stannous chloride (50 gr.) and glacial acetic acid (190 c.c.) was heated in a water bath at 50–60°C. with frequent shaking. The original substance disappeared in one hour but the heating was continued for 2.5 hours longer, hydrogen chloride being led in all the time. The solvent was then removed by distillation in a vacuum[18] and the residue thus obtained, made alkaline and extracted with ether. The ethereal residue, 8.5 gr., quickly set to a mass of crystals, which on two crystallizations from alcohol gave almost colourless prims, 6.5 gr., melting at 163–164°C. (Found: C = 85.5; H = 6.3. $C_{24}H_{20}N_2$ requires C = 85.7; H = 5.9%). The separation of the crystals from alcohol proceeded very slowly. The substance should be colourless when pure, but perfectly colourless crystals are difficult to obtain owing to oxidation. The hydrochloride as well as the sulphate of 2, 2′-diamino-6, 6′-diphenyl diphenyl are very difficultly soluble in water. Attempts to resolve the diamino-compound into optical isomers with *d*-tartaric, *d*-camphorsulphonic and *d*-bromocamphorsulphonic acids have been unsuccessful.

4, 5-Diphenyl Carbazol (XXXVI). 2, 2′-Diamino-6, 6′-diphenyl diphenyl (2 gr.) and 2n HCl (36 c.c.) were heated in a sealed tube in the atmosphere of carbon dioxide at about 200°C. for 7 hours. The brown mass thus obtained, on three crystallizations from ethyl alcohol, yielded colourless needles, 0.8 gr., which melted at 145–146°C. (Found: C = 90.0; H = 6.0; N = 4.4. $C_{24}H_{17}N$ requires C = 90.3; H = 5.3; N = 4.4%).

(C) *Decomposition of the Tetrazonium Sulphate* (XXIII) *obtained from 2, 2′-Diamino-6, 6′-diphenyl Diphenyl* (XVI).

The solution obtained by tetrazotizing 2, 2′-diamino-6, 6′-diphenyl diphenyl was decomposed under varied conditions: the decomposition was performed (i) at 100°C. in absence of copper powder, (ii) at 60–70°C. without the use of copper powder, (iii) at 40–45°C. in presence of copper powder and (iv) at ordinary temperature (5–15°C.) in absence of copper powder. It was found that 4, 5, 9, 10-dibenzopyrene (XXIV) was produced in each experiment with the yields varying from 36 to 40 per cent. of the theoretical, the other possible product, 4, 5-diphenyl diphenylene oxide (XXV) being

(18) The removal of the solvent must not be carried out under ordinary pressure, as in th at case the product is darkened considerably by oxidation.

isolated only from the products obtained in (i) and (ii). 2, 2′-Dihydroxy-6, 6′-diphenyl diphenyl (XXVI) was found to be present only in the products obtained in (i). Possibly the latter (XXVI) might have been produced in the other experiments but its yield must have been very poor. The yields of the three substances obtained in the four experiments are tabulated below, the figures representing the percentages of the theoretical yields calculated on the 2, 2′-diamino-6, 6′-diphenyl diphenyl employed.

	(i)	(ii)	(iii)	(iv)
4, 5, 9, 10-dibenzopyrene	38%	40%	40%	36%
4, 5,-diphenyl diphenylene oxide	30	12	0	0
2, 2′-dihydroxy-6, 6′-diphenyl diphenyl	5	0	0	0

The decomposition of the tetrazonium salt solution occurred even at ice-cold temperatures yielding the dibenzopyrene but the reaction velocity was very small. A feature in the decomposition of the tetrazonium salt was that the addition of copper powder to it had no effect to promote the decomposition as used to be the case in many diazonium salts. The only way to accelerate the reaction was to apply heating. The experiments were carried out as follows.

Experiment (i).—A suspension of powdered 2, 2′-diamino-6, 6′-diphenyl diphenyl (2.0 gr.) in a 15 per cent. sulphuric acid solution (25 gr.) was well agitated at 40–50°C. until completion of the salt formation. It was then cooled with ice water and treated with sodium nitrite (0.9 gr.). The very difficultly soluble sulphate of the base gradually disappeared forming after half an hour's agitation an almost clear solution. After filtration, the clear solution was poured into hot water in a beaker heated with boiling water bath. A short time later a vigorous decomposition took place yielding a dark gray precipitate which was collected and washed with water. The precipitate thus obtained, 1.9 gr. was found to contain the three substances, 4, 5, 9, 10-dibenzopyrene (0.66 gr.), 4, 5-diphenyl diphenylene oxide (0.55 gr.) and 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl (0.05 gr.), which were separated as described on p. 72–73.

Experiment (ii).—The tetrazonium sulphate solution prepared from 2, 2′diamino-6, 6′-diphenyl diphenyl in the same way as in the experiment (i) was heated without adding copper powder at 60–70°C. In this way 1.0 gr. of the diamino-compound gave 0.79 gr. of the precipitate from which 0.36 gr. of the dibenzopyrene (XXIV) and 0.12 gr. of 4, 5-diphenyl diphenylene oxide were obtained.

Experiment (iii).—The tetrazotized solution of 2, 2′-diamino-6, 6′-diphenyl diphenyl (1.0 gr.) was heated in presence of copper powder at 40–45°C. for two hours, at the end of which the reaction was complete.

The yield of the dibenzopyrene was 0.36 gr. Neither 4, 5-diphenyl diphenylene oxide nor 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl was produced.

Experiment (iv.)—The tetrazonium sulphate solution obtained in the same way as before was allowed to decompose at room temperature (5–15°C.). The decomposition proceeded very slowly with separation of bluish green precipitate. From time to time a test portion was acted on an alkaline β-naphtol solution. It was thus found that no less than a month was required to complete the reaction. That the decomposition is very considerably hastened by heating will be seen from the fact that, as stated in the experiment (ii), it was completed at 40–45°C. in two hours. From 1 gr. of 2, 2′-diamino-6, 6′-diphenyl diphenyl, 0.32 gr. of 4, 5, 9, 10-dibenzopyrene was obtained. As in the experiment (iii), 4, 5-diphenyl diphenylene oxide and 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl were not found among the products.

4, 5, 9, 10-Dibenzopyrene (XXIV). As described above, this compound was formed in the almost equal yields in the experiments (i), (ii), (iii) and (iv). In the following are described the method which was used for the separation of the three substances produced in the experiment (i).

An attempt was first made to extract the decomposition product (1.9 g., p. 71) obtained in the experiment (i) which contains the three substances (XXIV), (XXV) and (XXVI) with ethyl alcohol in which 4, 5, 9, 10-dibenzopyrene (XXIV) alone is insoluble. But as the dibenzopyrene was in such a fine state that it passed freely through the filter the solvent was removed and the residue dis olved in boiling benzene (600 c.c.) and concentated into a small bulk (60 c.c.). 4, 5, 9, 10-Dibenzopyrene thus obtained, 0.66 gr., was, though somewhat brown, almost pure as was evidenced by the fact that it showed no change in appearance at 350°C. It was purified by distillation under reduced pressure (4 mm.) and then by crystallization from benzene. It formed lustrous minute crystals with faintly yellowish shade, which melted without decomposition sharply at 353–355°C. (Found: C = 95.3; H = 4.7. $C_{24}H_{14}$ requires C = 95.4; H = 4.6%). 4, 5, 9, 10-Dibenzopyrene is insoluble or very difficultly soluble in usual organic solvents except boiling benzene in which it is slightly soluble. Thus in order to dissolve 1.0 gr. of the hydrocarbon, it must be boiled for a long time with 900–1000 c.c. of benzene.

The benzene filtrate separated from 4, 5, 9, 10-dibenzopyrene which contained 4, 5-diphenyl diphenylene oxide and 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl was used for the isolation of these substances as described below.

4, 5-Diphenyl Diphenylene Oxide (XXV). The benzene solution separated from 4, 5, 9, 10-dibenzopyrene as described above was evaporated off and the residue thus obtained extracted with ether. Some insoluble substance (0.06 gr.) was removed and the clear solution shaken with a dilute

potassium hydroxide solution. The alkaline layer was used for the isolation of 2, 2′-dihydroxy-6, 6′-diphenyl diphenyl as will be described later. The ethereal layer was then evaporated into dryness and the dark residue, 0.77 gr. crystallized from ethyl alcohol (50 c.c.). The crystals (0.45 gr.) thus obtained, though coloured dark, formed uniform needles melting at 150–153°C. and found to be fairly pure 4, 5-diphenyl diphenylene oxide. It was purified first by vacuum distillation and then by crystallization from ethyl alcohol. The colourless needles thus obtained melted at 154–155°C. (Found: C = 89.8; H = 5.5. $C_{24}H_{16}O$ requires C = 90.0; H = 5.0%). From the alcoholic mother liquors a further crop (0.10 gr.) of the 4, 5-diphenyl diphenylene oxide was obtained, making its total yield to about 0.55 gr. It is easily soluble in ether and fairly soluble in boiling ethyl alcohol but difficultly so in cold alcohol.

2, 2′-Dihydroxy-6, 6′-diphenyl Diphenyl (XXVI). This substance was contained in the alkaline layer separated from the ethereal layer containing 4, 5-diphenyl diphenylene oxide (see above). The alkaline solution on acidification precipitated this compound which was extracted with ether. As the ethereal residue was found to contain a trace of something which was insoluble in alkaline solution, it was treated with a warm aqueous potassium hydroxide solution and the insoluble matter filtered off. The filtrate was acidified, extracted with ether, and the ethereal residue recrystallized from petroleum ether (b.p. 60–70°C.). It formed colourless, slender needles melting at 145–147°C. The yield was 0.05 gr. The substance thus obtained was not quite pure (Found: C = 82.92; H = 5.85. $C_{24}H_{18}O_2$ requires C = 85.2; H = 5.3%), but there is no other alternative formula possible.

2, 2′-Dihydroxy-6, 6′-diphenyl diphenyl is easily soluble in ether, fairly soluble in ethyl alcohol and slightly soluble in boiling petroleum ether (b.p. 60–70°), but practically insoluble in cold petroleum ether.

(D) *Decomposition of the Tetrazonium Sulphates obtained from 2, 2′-Dimethyl-6, 6′-diaminodiphenyl and 2, 2′-Diaminodiphenyl.*

2, 2′-Dimethyl-6, 6′-dihydroxydiphenyl (XXXIV). This compound was obtained as the only isolable product when the tetrazotized solution of 2, 2′-dimethyl-6, 6′-diaminodiphenyl was decomposed. It was produced by effecting the decomposition either on heating or at ordinary temperature, but in the latter case its yield was only a trace.

A solution of 2, 2′-dimethyl-6, 6′-diaminodiphenyl, (4.24 gr.) in conc. sulphuric acid (12.0 gr.) and water (60 c.c.) was treased with sodium nitrite (2.9 gr.).

The tetrazonium sulphate solution was then poured into a beaker which was immersed in a boiling water bath. The decomposition was soon complete, a bluish dark precipitate being separated. The precipitate, 4.5 gr., was then submitted to steam distillation, a time-consuming work owing to the high b.p. of the product. The distillate was shaken with ether and the ethereal residue, about 1.5 gr., on crystallization from benzene (10 c.c.) gave 0.9 gr. of large colourless plates melting at 161–162.5°C. The m.p. was not altered by further crystallization (Found: C = 78.6; H = 7.0. $C_{14}H_{14}O_2$ requires C = 78.5; H = 6.5%).

2, 2′-Dimethyl-6, 6′-dihydroxydiphenyl is easily soluble in aqueous alkaline solution. It was found that, compared with the tetrazonium sulphates obtained from 2, 2′-diaminodiphenyl (see below) and 2, 2′-diamino-6, 6′-diphenyl diphenyl (see p. 72), the tetrazonium sulphate prepared from 2, 2′-dimethyl-6, 6′-diaminodiphenyl was very much less stable, its decomposition being completed at about 25°C. in two days or so.

Diphenylene Oxide (XXII). As stated in the introduction Täuber obtained this substance in a 70 per cent. yield by heating the tetrazonium salt solution made from 2, 2′-diaminodiphenyl. It was found that as described below the same compound was produced in a 60 per cent. yield by allowing the tetrazonium salt to decompose at ordinary temperature.

2, 2′-Diaminodiphenyl (3.68 gr.) dissolved in conc. H_2SO_4 (12.0 gr.) and water (60 c.c.) was treated with a solution of sodium nitrite (2.9 gr.) in water and the resulting tetrazonium salt solution left to decompose at ordinary temperature (about 25°C.), until a test portion of the liquid reacted no more with an alkaline β-naphthol solution. The reaction was complete in 24 days. The darkish precipitate was filtered off and the dried product, 3.1 gr., distilled under diminished pressure. The distillate (2.1 gr.) boiling at 120–125°C./5 mm. quickly set to a mass of crystals which, after being powdered, was extracted with an aqueous alkaline solution, by which treatment however no appreciable loss was observed in the weight of the distillate, a fact which indicates the absence in the distillate of the other possible product, 2, 2′-dihydroxydiphenyl. In order to be sure on this point, the alkaline solution was acidified, but no precipitation occurred. Furthermore, the acidified solution was shaken with ether and the ethereal layer evaporated off, but there was no residue. As a matter of fact, the distillate obtained above was almost pure diphenylene oxide. The crystals on crystallization from alcohol-water gave colourless crystals melting at 85–86°C.

Chemical Department, Faculty of Engineering,
Kyushu Imperial University, Fukuoka.

SOME CHEMICAL CHANGES OF MUSCLE PROTEINS IN CANNING.*

By Yuzuru OKUDA and Kazuo YAMAFUJI.

Received November 24th, 1933. Published February 28th, 1934.

Some changes take place in proteins and extractive matters of meats simply by heating in the case of canning. In this paper it is described on the study of the decomposition occurring in the muscle proteins.

The materials were prepared from muscles by removing substances soluble in water, alcohol and ether. The solutions of various pH values were added to the muscle proteins. The mixtures were sealed tightly in glass tubes and heated at 120–140°C. The purpose for adding the solutions of various pH values to the muscle proteins and heating them is to find out the changes of the muscle proteins in different hydrogen ion concentrations, and for using of glass-tubes is to learn the chemical changes free from the influence of any metallic can-materials.

(1) Changes of the Hydrogen Ion Concentrations. As the concentration of hydrogen ion of the contents of cans has great influences on etching the tin plated iron sheet of cans and on the chemical changes of the contents which occur during preservation, the experiments were carried out by the electric method for ascertaining the variation of pH value of muscle proteins by heating.

The proteins of whale, rabbit, hen, sea-bream, yellow-tail, carp, bonito, cuttle-fish and spiny-lobster were closen as experimental materials. Either a slightly acidic or alkaline solution or distilled water was added to the proteins before heating. The results of experiments always showed the tendency of pH to approach towards the neutral value. For example, when the muscle proteins of whale were heated at the pH values of 3.4, 6.2 (adding water) and 8.5, the pH changed to 4.5, 6.6 and 8.1 respectively. Thus, it is considered that these variations were probably due to the volatile basic and acidic substances, such as ammonia and hydrogen sulphide, as well as to the soluble amphoteric electrolytes, such as polypeptide and amino acid produced while heating.

(2) Changes of the Form of Nitrogen. When the muscle proteins of whale, rabbit, cow, hen and mackerel were heated in distilled water at 150°C. for one hour, about 20 per cent. of their protein-nitrogen changed to

* This paper was already published more precisely in Japanese in Journal of the Society of Agricultural Chemistry of Japan, **9** (1933), 835.

the forms of peptone, peptide, amino acid and ammonia. The formation of these soluble nitrogenous substances may cause a speedy putrefaction to the opened canned meat. The distribution of nitrogen of the muscle proteins after heating is shown in Table 1.

Table 1.

	In per cent. of dry matter					In per cent. of total N			
	Total-N	Protein-N	Amino-N	Ammonia-N	Residual-N	Protein-N	Amino-N	Ammonia-N	Residual-N
Whale	16.35	13.52	0.52	0.09	2.22	82.69	3.18	0.55	13.58
Rabbit	15.88	11.35	0.78	0.02	3.73	71.47	4.91	0.13	23.48
Cow	16.52	14.31	0.43	0.29	1.49	86.62	2.60	1.76	9.00
Hen	16.86	13.90	0.52	0.31	2.13	82.44	3.08	1.83	12.63
Mackerel	16.81	14.18	0.45	0.34	1.84	84 35	2.68	2.04	10.95

(3) Changes in the Elementary Composition of Muscle Proteins. In order to ascertain what changes take place in the elementary composition of muscle proteins through heating under pressure, and to find out the effects of pH values upon these changes, the muscle proteins of whale, rabbit, hen and sea-bream were heated at the initial pH values of 3.4, 6.2 and 8.5. The results of experiments showed the decrease of their nitrogen and sulphur contents and the amounts of the decrease were particularly marked when the substances were heated in the solutions having the greater values of pH. The results are given in Table 2.

Table 2.

		C	H	N	S	P
Whale	Original protein	51.60	6.91	16.48	0.74	0.085
	Protin heated at pH 3.4	51.88	6.88	16.28	0.74	0.076
	pH 6.2	51.93	6.87	15.97	0.73	0.086
	pH 8.5	52.54	6.85	15.57	0.70	0.071
Rabbit	Original protein	52.32	7.12	16.30	0.86	0.093
	Protein heated at pH 3.4	52.47	7 13	16.11	0.86	0.078
	pH 6.2	52.55	7.11	15.92	0.83	0.092
	pH 8.5	52.99	7.05	15.38	0.84	0.069

Table 2.—(*Concluded*)

		C	H	N	S	P
Hen	Original protein	52.53	7.18	16.76	0.85	0.093
	Protein heated at pH 6.2	52.88	7.14	16.33	0.84	0.094
Sea-bream	Original protein	52.79	7.08	16.42	0.95	0.095
	Protein heated at pH 6 2	52.92	7.03	16.07	0.93	0.093

(4) Generation of Ammonia and Hydrogen Sulphide. The results of experiments with four kinds of muscle proteins revealed the fact that both NH_3 and H_2S were generated in larger quantities when they were heated in the solutions having the greater values of pH. This fact agrees with the result of the elementary analysis. When the material of the tin is bad and iron dissolves in the liquid contained in the can, then sulphide of iron precipitates and causes the deterioration and blackening of the canned meats. The amounts of NH_3 and H_2S in mg. generated from 100 gr. of muscle proteins are shown in Table 3.

Table 3.

NH_3 (mg. in 100 gr. of proteins)

pH before heated	Whale	Rabbit	Hen	Sea-bream
3.4	0.15	0.21	—	—
6.2	0.58	1.76	1.36	1.88
8.5	28.44	36.89	—	—

H_2S (mg. in 100 gr. of proteins)

pH before heated	Whale	Rabbit	Hen	Sea-bream
3.4	0	0	—	—
6.2	9.37	1.14	0.87	15.62
8.5	27.72	12.89	—	—

(5) Changes of the Amounts of Arginine, Histidine, Lysine, Cystine, etc. In order to learn how the distributions of arginine, histidine, lysine, cystine and other nitrogen in the muscle proteins of whale, rabbit, hen and sea-bream change by heating, the quantitative analyses were carried out by the Van Slyke method before and after the heating. The proteins were heated at three different values of pH to ascertain the effects of solutions of various pH upon the proteins. The results are as follows (Table 4).

Table 4.

	Total-N	Ammonia-N	Melanine-N	Cystine-N	Arginine-N	Histidine-N	Lysine-N	Monoamino-N	Nonamino-N
Whale									
In per cent. of protein									
Original protein	16.48	0.69	0.33	0.29	2.49	2.20	1.34	8.02	1.18
Protein heated at pH 3.4	16.28	0.59	0.45	0.16	2.59	2.28	1.16	7.79	1.23
pH 6.2	15.97	0.55	0.44	0.14	2.36	2.36	1.26	7.66	1.21
pH 8.5	15.57	0.45	0.43	0.10	2.49	1.96	1.34	7.45	1.35
In per cent. of total N									
Original protein	100	4.29	2.02	1.45	15.08	13.37	8.15	48.66	7.15
Protein heated at pH 3.4	100	3.62	2.79	1.04	15.94	14.03	6.48	47.84	7.67
pH 6.2	100	3.42	2.73	0.87	14.77	14.79	7.88	47.95	7.57
pH 8.5	100	2.91	2.73	0.64	15.97	12.59	8.62	47.85	8.64
Rabbit									
In per cent. of protein									
Original protein	16.30	0.74	0.36	0.19	2.49	1.93	1.26	8.17	1.15
Protein heated at pH 3.4	16.11	0.73	0.46	0.15	2.58	1.92	0.94	7.82	1.41
pH 6.2	15.92	0.50	0.38	0.13	2.34	2.17	1.15	7.89	1.34
pH 8.5	15.38	0.39	0.43	0.10	2.49	1.75	1.23	7.59	1.41
In per cent. of total N									
Original protein	100	4.56	2.17	0.18	15.28	11.85	7.74	50.15	7.06
Protein heated at pH 3.4	100	4.55	2.83	0.92	16.04	12.53	6.04	48.45	8.78
pH 6.2	100	3.81	2.36	0.79	14.41	13.60	6.92	49.61	8.43
pH 8.5	100	2.57	2.77	0 65	16.16	11.38	8.02	49.32	9.18

Table 4.—(*Concluded*)

	Total-N	Ammonia-N	Melanine-N	Cystine-N	Arginine-N	Histidine-N	Lysine-N	Monoamino-N	Nonamino-N
Hen									
In per cent. of protein									
Original protein	16.76	1.10	0.48	0.18	2.71	1.97	1.36	8.19	0.76
Protein heated at pH 6.2	16.33	0.89	0.63	0.14	2.55	2.04	1.15	7.97	0.97
In per cent. of total N									
Original protein	100	6.58	2.85	1.07	16.14	11.73	8.12	49.60	4.53
Protein heated at pH 6.2	100	5.42	3.88	0.85	15.61	12.51	7.04	48.78	5.95
Sea-bream									
In per cent. of protein									
Original protein	16.42	0.77	0.36	0.28	2.54	2.24	1.47	8.35	0.42
Protein heated at pH 6.2	16.07	0.45	0.48	0.12	2.46	2.36	1.37	8.20	0.51
In per cent. of total N									
Original protein	100	4.70	2.17	1.69	15.46	13.61	8.92	50.83	2.55
Protein heated at pH 6.2	100	3.43	2.99	0.77	14.68	14.71	7.93	50.42	3.17

It was found that the total nitrogen, ammonia and cystine nitrogen always decrease by heating, and the higher the value of pH the greater the rate of the decrease, while melanine nitrogen generally increases. The amounts of cystine, arginine, histidine and lysine contained in the proteins before and after heating were calculated in per cent. from the above results.

Table 5.

		Cystine	Arginine	Histidine	Lysine
Whale	Original protein	2.49	7.74	8.12	6.99
	Protein heated at pH 3.4	1.37	8.04	8.41	6.05
	pH 6.2	1.20	7.33	8.71	6.57
	pH 8.5	0.86	7.74	7.23	6.99
Rabbit	Original protein	1.63	7.74	7.11	6.57
	Protein heated at pH 3.4	1.29	8.02	7.09	4.90
	pH 6.2	1.11	7.27	8.01	6.00
	pH 8.5	0.86	7.74	6.46	6.41

Table 5.—(*Concluded*)

		Cystine	Arginine	Histidine	Lysine
Hen	Original protein	1.54	8.42	7.27	7.09
	Protein heated at pH 6.2	1.20	7.92	7.53	6.00
Sea-bream	Original protein	2.40	7.89	8.27	7.67
	Protein heated at pH 6.2	1.03	7.64	8.71	7.14

According to Table 5, the quantities of cystine, arginine, histidine and lysine contained in the proteins after heating showed a tendency of decrease, as compared with those contained in the original proteins. Such tendencies were remarkable on cystine at the higher pH before heating and on lysine at the lower pH.

(6) Changes of Tyrosine and Tryptophane. The quantities of tyrosine and tryptophane contained in the muscle proteins of whale, hen, rabbit, yellow-tail, carp, bonito, sea-bream, cuttle-fish and spinylobster were determined before and after heating. The amounts of those amino acids decreased by heating, but very little, as it is obvious in Table 6.

Table 6.

Proteins	Tyrosine		Tryptophane		pH	
	Before heating	After heating	Before heating	After heating	Before heating	After heating
Whale	5.11	4.97	1.51	1.32	6.2	6.6
Hen	4.81	4.78	1.58	1.59	6.2	6.6
Rabbit	5.49	5.27	1.68	1.57	6.2	6.6
Yellow-tail	4.97	4.69	1.70	1.62	6.51	6.54
Carp	4.71	4.53	1.50	1.47	5.02	5.92
Bonito	4.84	4.60	1.63	1.46	7.17	6.65
Sea-bream	5.00	4.74	1.63	1.56	6.37	6.51
Cuttle-fish	4.83	4.71	1.37	1.29	4.67	5.57
Spiny-lobster	5.05	4.81	1.46	1.34	3.98	5.29

(7) Change of Proline. The experiments were carried out by using each 40 gr. of gelatine to find out the difference between the quantities of

proline contained in the materials before and after heating. It was observed that there was almost no difference between them, and when the pure solution of proline was heated, there was no detectable decomposition. Therefore the amount of proline in muscle proteins may probably be the same.

(8) **Changes of the Forms of Cysteine, Cystine and Sulphur.** When the solutions of pure cystine and cysteine were heated under the different pH, a part of the one always changed into the other. That is, when the solution of any of the two acids was heated, it was found that the solution contained the both acids, but the sum of the two quantities always decreased. The results of the experiments are as follows:

Table 7.

pH, before heating	Sample	Used, mg.	Found, mg.		Sum
			Cysteine	Cystine	
1.7	Cysteine	37.5	32.0	3.8	35.8
4.8	Cystine	45.6	2.9	39.9	42.8
6.8	Cysteine	25.1	9.4	6.6	16.0
6.8	Cystine	22.6	2.7	17.1	19.8
8.3	Cysteine	25.8	5.1	5.3	10.4
8.6	Cystine	25.0	2.7	16.2	19.2

The muscle proteins of sea-bream were heated at pH 6.1 (a) and 9.2 (b), and the forms of sulphur were determined. The results obtained are as follows:

Table 8.

Mg. per cent. of protein	Total S	Cysteine	Cystine	H_2S S	Sulphide S	Sulphate S	Soluble-organic S
Before heating	690	660	190	—	—	—	—
After heating (a)	—	490	200	6.6	0.4	18	96
„ „ (b)	—	440	110	20.9	4.6	30	103

In per cent. of total S	Total S	Cysteine S	Cystine S	H_2S	Sulphide S	Sulphite S	Soluble-organic S	Protein S
Before heating	100	26.0	7.2	—	—	—	—	—
After heating (a)	—	19.0	7.5	0.9	0.06	2.6	14.0	82.4
„ „ (b)	—	17.5	4.3	2.9	0.7	4.3	15.0	77.1

Namely, when it was heated in alkaline solutions, the decompositions of cysteine and cystine were especially considerable, and hydrogen sulphide and other sulphides were formed in large quantities.

In conclusion the authors wish to express their thanks to Messrs. U. Endo, S. Nagatake, S. Shigematsu and K. Katai for their analytical works and also to "Hatutori-Hokokuwai" for a research grant which has defrayed a part of the cost of this investigation.

Summary.

(1) The muscle proteins of some hens, various fishes and certain animals were prepared as samples for the purpose of studying what changes take place in the muscle proteins at the time of canning meats under pressure and heating. The materials were sealed in glass-tubes and heated at 130-140°C. for one hour, and changes of materials were studied.

(2) The hydrogen ion concentration of all of the proteins showed a tendency to approach toward the neutral point.

(3) About 20 per cent. of the protein nitrogen was transformed by heating to peptone, peptide, and amino acid nitrogens. The formation of soluble nitrogen compounds, such as these, is considered to cause a speedy putrefaction of contents of an opened can.

(4) As the results of elementary analyses of carbon, hydrogen, nitrogen, sulphur and phosphorus, it was found that the quantities of nitrogen and sulphur contained in the proteins generally decreased by heating, and the changes were more marked the higher the values of pH. There was no appreciable change in phosphorus when the solution was neutral, but its amount decreased when the solution was acidic or alkaline, and hence the percentage of carbon increased.

(5) The quantities of NH_3 and H_2S generated by heating were greater in proportion to the values of pH of the solutions. This result explains the fact that, when the tin of cans are bad and the pH of the contents is high, the contents of the can deteriorate more readily and the colour changes to black.

(6) As the results of the analyses of the proteins by the Van Slyke method, the decrease of the total nitrogen, ammonia nitrogen and cystine nitrogen and the increase of melanine nitrogen were detected especially when the pH value increased. The quantities of cystine, arginine, histidine and lysine contained in the materials showed a tendency of decrease in all

three cases and the same tendencies were very remarkable on cystine at the higher value of pH and on lysine at the lower.

(7) Tryptophane by the May-Rose method and tyrosine by the Folin-Denis method were quantitatively analyzed, and the decreases of these substances by heating were very insignificant.

(8) The test for proline was made by the Fisher-Bechner method, but no decomposition by heating was observed.

(9) Cysteine and cystine were analyzed quantitatively by the Okuda-Katai method, and it was found that a part of any one of these acids always changed to the other acid by heating. But the sum of the two always decreased, and the decomposition of both of these acids was remarkable at the higher value of pH, and the decomposition of cysteine was greater than that of cystine.

(10) A part of the protein-sulphur changed by heating to hydrogen sulphide, other sulphides, sulphuric acid and soluble organic sulphur, and the quantities of these substances generated were greater at the higher pH of the solutions, as in the case of the decompositions of cysteine and cystine.

The Department of Agricultural Chemistry,
Kyushu Imperial University, Fukuoka.

GLUCOSULFATASE. IX.
ON THE SPECIFICITY OF THE ENZYME.

By Tokuro SODA.

Received December 20th, 1933. Published February 28th, 1934.

The name "Glucosulfatase" has been provisionally given to our sulfatase because it seemed to hydrolyse most easily glucose-mono-sulphate. At that time the enzyme-solution had been prepared from *Eulota*, and had only a small activity, consequently the experimental result was somewhat obscure.[1] Meanwhile we have found in *Charonia lampas* a very suitable source of the enzyme[2] and we know now that a very active enzyme can be obtained from its liver by a relatively simple method of purification.[3][4] Glucosulfatase has always been found together with phenosulfatase, but we

(1) This Bulletin, **6** (1931), 258.
(2) This Bulletin, **8** (1933), 65.
(3) *J. Chem. Soc. Japan*, **54** (1933), 377.
(4) This Bulletin, **8** (1933), 148.

have already pointed out the facts which prove that these two enzymes must be different with each other: that the former looses its activity in the alkaline medium while the latter does not,[4] and that each has different tendency toward the adsorption of charcoal.[5] Moreover we have recently succeeded to obtain a solution of glucosulfatase almost free from phenosulfatase.[6] Therefore, it is now quite certain that our enzyme belongs to a new type of sulfatase. We do not know yet, however, whether the name "Glucosulfatase" has been properly adopted or not, for its specificity was tested only with a few substrates at the beginning of this work.[1]

It would be now an urgent problem to settle the specificity of our enzyme and to give it an appropriate name. For this purpose we prepared following aliphatic sulphuric acid esters and examined their hydrolysability by the enzyme: ethyl sulphate, mannite-tetra-sulphate, chondroitinsulphuric acid, glucose-6-mono-sulphate, α-methyl-glucoside-mono-sulphate, mono-acetoneglucose-6-mono-sulphate, diacetoneglucose-3-mono-sulphate, fructose-tri-sulphate, galactose-di-sulphate, galactose-tetra-sulphate, mannose-mono- and di-sulphate, sucrose-di-sulphate and the same inverted, maltose-mono-sulphate, starch-di-sulphate. Not many sulphuric acid esters of sugars are known at present and we have had to synthesize some of them for the first time in this laboratory. The chemical constitution of these esters are mostly unknown, so any theoretical deduction from this experiment will be reserved. Fortunately, however, glucose 6-mono-sulphate has been found, as ever, to be the most easily hydrolysable substrate of all. Therefore the name "Glucosulfatase" still seems to be adequate.

The experiments were carried out side by side with those described in the communications V[4] and VII,[5] so that enzyme solution were common to each other, and the experimental procedure was about the same as before. The reaction mixtures had following composition.

Substrate solution (with $BaCl_2$)	25 c.c.
Enzyme solution	25 c.c.

Chloroform (as an antiseptic) and $BaCO_3$ (as a buffer) were added.

10 c.c. of the above mixture were pipetted out, filtered with charcoal and the clear filtrate was decomposed with HCl; H_2SO_4 thus set free was weighed as $BaSO_4$.

Exp. I. The final purification of enzyme was done with $Al(OH)_3$-gel (Communication V. Exp. B. III). Solutions of substrates were about in the same molar concentration as free acids (0.07 Mol.).

(5) *J. Chem. Soc. Japan*, **54** (1933), 1069.
(6) It will be reported in "Glucosulfatase X".

Exp. II. Enzyme solution was further purified with charcoal after the treatment with $Al(OH)_3$-gel (Communication V. Exp. B. IV).

Exp. III. The enzyme solution was prepared according to the direction given in the communication VII, i.e. dil. NH_4OH is added to the crude autolysate from dried liver of *Charonia* and subsequently treated with Na_2SO_4 and $BaCl_2$ solution, pH being kept at 9.5–10.0. By such a treatment most of the phosphate which seems to inhibits the action of glucosulfatase, was precipitated and the activity of the enzyme increased. Further treatment was the same as Exp. II.

Results of the experiments are tabulated below.

Exp. I.

Substrate	$BaSO_4$ mg.			% of hydrolysis	
	Initial	2 days	10 days	2 days	10 days
Glucose-SO_3-Ba	83.2	27.6	25.4	66.8	69.5
Galactose-$(SO_3)_2$-Ba	139.6	109.2	81.6	21.8	41.6
Galactose-$(SO_3)_4$-Ba	291.2	224.3	211.8	23.0	27.3
Sucrose-$(SO_3)_2$-Na (inverted)	87.8	57.3	52.4	34.8	40.3

Exp. II.

Substrate	$BaSO_4$ mg.		% of hydrolysis
	Initial	2 days	
Glucose-SO_3-Na	99.5	20.9	79.1
α-Methylglucoside-SO_3-Ba	94.6	45.9	56.5
Sucrose-$(SO_3)_2$-Ba (inverted)	82.6	49.4	40.1
Galactose-$(SO_3)_4$-Ba	78.4	58.2	38.5
Maltose-SO_3-Ba	93.7	61.1	34.8
Sucrose-$(SO_3)_2$-Ba	76.5	69.2 (3 days)	9.5
Diacetoneglucose-SO_3-Ba	108.5	100.2	7.6
Mannite-$(SO_3)_4$-Ba	100.1	98.7	1.4
Chondroitinsulphuric acid (Na)	121.0	120.6	0.3
Monoacetoneglucose-SO_3-Ba	80.1	80.0	0.0
Fructose-$(SO_3)_3$-K	96.5	96.5	0.0
Ethyl-SO_3-Ba	149 3	149.5	0.0

Exp. III.

Substrate	$BaSO_4$ mg.		% of hydrolysis
	Initial	2 days	
Glucose-SO_3-Ba	113.4	9.1 (1 day)	92.0
Mannose-SO_3-Ba	200.8	60.9	69.7
Sucrose-$(SO_3)_2$-Ba	108.3	91.8	15.2
Starch-$(SO_3)_2$-K [7]	(221.5)	—	1.0

The preparation of substrates.

(1) Glucose-6-mono-sulphate: Soda, this Bulletin, 8 (1933), 37.

(2) Galactose-tetra-sulphate: Akamatsu, *Biochem. Z.*, **142** (1923), 181.

(3) Diacetone-3-mono-sulphate: Ohle, *Biochem. Z.*, **136** (1923), 428.

(4) Monoacetone-6-mono-sulphate: ibid.

(5) Chondroitinsulphuric acid: Jorpes, *Biochem. Z.*, **204** (1929), 354. (prepared from cartilage).

(6) Starch-di-sulphate: Tamba, *Biochem. Z.*, **141** (1923), 274.

(7) Mannite-tetra-sulphate: Favre, *Ann. chim. phys.* (3) **11** (1844), 77. Favre had obtained di-ester, but in my case the product was found to be tetra-ester notwithstanding the same direction was followed. 3.6 Gr. of Ba-salt was obtained from 21 gr. mannite; Ba-content: 34.8%, calculated for $C_6H_8O_6(SO_3)_4Ba_2$: 35.25%.

(8) Sucrose-di-sulphate: Soda, this Bulletin, 9 (1934), 1.

(9) Sucrose-di-sulphate (inverted); The solution of the free acid of (7) was kept for few days at room temperature and then neutralized with $BaCO_3$. By such a treatment the disaccharide is splitted into a mixture of hexose-sulphate.

(10) α-Methylglucoside-mono-sulphate: The same direction as (1) was applied to α-methylglucoside, but without fermentation with yeast. Yield: 8 gr. as Ba-salt from 20 gr. of glucoside. Content of Ba: 18.45%, calculated from $(C_6H_{10}O_6CH_3SO_3)_2Ba \cdot C_2H_5OH$: 18.7%.

(11) Galactose-di-sulphate: Galactose was, as glucose, treated in pyridin with chlorosulphonic acid. Its crude Ba-salt was purified by crystallizing it as brucine-salt, because the residual galactose could not be fermented off by the ordinary baker's yeast. From 15 gr. galactose 16 gr.

(7) As this substrate is precipitated by Ba-ion, the hydrolysed H_2SO_4 was estimated by alkalimetry (instead of $BaCO_3$ Na-acetate was used as a buffer pH: 5.4).

crude Ba-salt, and from the latter 6 gr. crystalline brucine-salt were obtained. Sulphur content of brucine salt: 5.65%; calculated from $C_6H_{10}O_6(SO_3\text{-brucine})_2$: 5.67%. $[\alpha]_{5461} = -8.3° \rightarrow -10.1°$ (c = 2.11 in 10% alcohol). Ba-salt used for the experiment was prepared from this brucine salt. Galactose-meno-sulphate could not be obtained.

(12) Maltose-mono-sulphate: 20 gr. maltose dissolved in pyridin was sulphonated with chlorosulphonic acid and by exactly the same treatment as in the case of glucose its Ba-salt was prepared. Yield: 7 gr. The content of Ba: 12.5%; calculated from $(C_{12}H_{21}O_{11}SO_3)_2Ba \cdot C_2H_5OH$: 12.8%. $[\alpha]_{5461} = +97.0°$ (c = 3.36). Its reducing power was increased about 1.44 times by heating its acidic solution at 100°C. for 4 hours (estimated by Hagedorn-Jensen-Hanes' method).

(13) Mannose-mono- and di-sulphate: The method of preparation was exactly the same as glucose-mono-sulphate. Ba-content of its Ba-salt was found to be 22.6% while the calculated value from $(C_6H_{11}O_6SO_3)_2Ba$ is 20.97%. Yield: 20 gr. 10 Gr. of the Ba-salt was changed into brucine-salt by usual way. Relatively insoluble salt of di-ester first crystallized out of its water-solution (about 1.6 gr.), and mono-ester, in the mother-liquor, crystallized out (15 gr.) when acetone was added in the hot solution. Analysis: Brucine-mannose-mono-ester $C_6H_{11}O_6SO_3H \cdot C_{23}H_{26}N_2O_4 \cdot H_2O$, found: 4.80% S; calculated 4.82%. $[\alpha]_{5461} = -14.26°$ (c = 1.825). Brucine-mannose-di-sulphate $C_6H_{10}O_6(SO_3H \cdot C_{23}H_{26}N_2O_4)_2$, found: 5.65% S; calculated: 5.67%.

(14) Fructose-tri-sulphate: Dried fructose (18 gr.) was dissolved in pyridin (20 c.c.) and mixed with an alcoholic solution of pyridin-sulphonic acid (20 gr. in 50 c.c.). Then the mixture was evaporated to syrup at 60–70°C. under reduced pressure and kept at 35°C. for 2 days. Again it was evaporated under the same condition until no more bubbles could be seen; then it was dissolved in cold water and treated with barium hydroxide until it became just a little alkaline. The excess of $Ba(OH)_2$ was precipitated with CO_2 and the solution was evaporated at 40°C. under reduced pressure until free from pyridin. A little excess of H_2SO_4 was added to it and by treating with PbO and subsequently by passing H_2S the free acid of the acid-ester was obtained as its aqueous solution. It was neutralized with KOH and fermented over night with yeast to remove free sugar. It was filtered, concentrated under reduced pressure and precipitated by adding about its 10 volumes of absolute alcohol. Yield was about 10 gr. According to the analysis of this K-salt the percentage of K was found to be 21.95% and 21.86%, and that of S 17.67% and 17.93%; whereas percentages calculated from the formula $C_6H_9O_6(SO_3K)_3$ are found to be K = 21.95% and S = 17.99%. $[\alpha]_{5461} = -5.4°$ (c = 3.03).

The present author owes to Mr. J. Yamazaki in preparing fructose-trisulphate, to Mr. W. Nagai, mono- and diacetoneglucose sulphate and as for the preparation of enzyme and the analytical work to Mr. F. Egami; he wishes here to express his thanks for their kind assistance. And his thanks are also due to the Imperial Academy of Science for being defrayed a part of the research cost.

Chemical Laboratory, Faculty of Science,
Tokyo Imperial University.

STUDIES OF THE RAMAN EFFECT. PART II. THE RAMAN EFFECT OF PHENYL-ACETATES, PHENYL-PROPIONATE, CINNAMATES, PHTHALATES, SALICYLATES AND PHENYLMETHYLCARBINOL.

By **Kichimatsu MATSUNO** and **Kwan HAN.**

Received December 5th, 1933. Published February 28th, 1934.

Introduction.

The Raman effects of a series of esters of benzoic acid and phenol esters of fatty acids have been recently studied.[1] In order to confirm the constitutive influences exerted on the frequencies attributable to the benzene ring, between mono- and diderivatives, and to study the influences exerted on the –C=O linkage and the valency frequencies, of the $-\overset{\|}{C}-O-R$ system, the Raman spectra of the following nine kinds of alkyl esters of aromatic acids, viz., methyl phenyl acetate, ethyl phenyl acetate, ethyl phenyl propionate, ethyl cinnamate, iso-propyl cinnamate, dimethyl phthalate, diethyl phthalate, methyl salicylate and ethyl salycilate, and also for the comparison, methyl phenyl carbinol have been studied in the present investigation. Kohlrausch and Pongratz[2] have shortly published the Raman spectra of dimethyl-phthalate and ethyl cinnamate. Their results are good agreement with ours, though the experimental data of ethyl cinnamate have not been thoroughly reported.

(1) This Bulletin, **8** (1933), 333.
(2) *Ber.*, (B) **66** (1933), 1–12.

Experimental.

The experiments were carried out with the same apparatus as described in our previous paper.[1] All the substances used were prepared in our laboratory by the following processes, excepting methyl salicylate.

Methyl and ethyl phenyl-acetates[3] were made from the dehydrated alcohols and phenyl-acetic acid (made in Japan) by the action of conc. sulphuric acid.

Ethyl phenyl-propionate[4] was prepared from dehydrated ethyl alcohol and phenyl-propionic acid which was obtained by reducing the cinnamic acid with natrium amalgam.

Ethyl and iso-propyl cinnamate[5] were prepared from the corresponding alcohols and cinnamic acid (m.p. 133°C.), by the action of conc. sulphuric acid or dry hydrochloric acid gas.

Di-methyl and di-ethyl phthalates[6] were prepared by boiling the corresponding absolute alcohols and phthalic acid in the presence of conc. sulphuric acid.

Ethyl salicylate[7] was prepared from the absolute alcohol and the acid by the action of hydrochloric acid gas. As to methyl salicylate, Kahlbaum's was used.

Phenyl methyl carbinol[8] was prepared from benzaldehyde by the action of magnesium methyl iodide, that is, the Grignard reagent.

For the simplification, the name of the substance, the number of the table (Tb. No.), the numbers of the Raman lines (n), the number of the plate (Pl. No.) and the conditions under which the spectra were taken, viz., breadth of the slit (St), electric current (C) working the mercury vapour lamp, temperature of the sample during the experiment (T) and the time of exposure (t), are tabulated.

(3) *Ber.*, **2** (1869), 208.
(4) *Ann.*, **137** (1866), 334.
(5) *Ber.*, **28** (1896), 3254.
(6) *Monat. Chem.*, **25** (1904), 1204.
(7) *Ann.*, **197** (1879), 17.
(8) *Ber.*, **31** (1898), 1003.

Table A.

No.	Substance	Tl. No.	n	Pl. No.	St. 10^{-2}mm.	C (amp)	$T°$ (C)	t (hours)
1	Methyl phenylacetate	I	42	78	7	2.8	19	7
				79	6	3.2	19	13
2	Ethyl phenylacetate	II	35	80	7	3.2	20	8
				86	6	3.2	20	13
3	Ethyl phenylpropionate	III	30	92	7	3.2	20	13
				94	6	3.2	20	15
4	Ethyl cinnamate	IV	72	52	7	2.8	23	10
				54	7	3.2	19	2
				55	6	3.2	19	4
5	Isopropyl cinnamate	V	46	105	6	2.8	21	4
				106	6	3.2	21	3
6	Dimethyl phthalate	VI	37	46	7	2.8	23	8
				51	6	3.2	19	13
7	Diethyl phthalate	VII	42	41	8	2.8	22	7
				45	6	3.2	19	12
8	Methyl salicylate	VIII	34	56	10	3.2	23	2
				57	7	3.2	23	7
9	Ethyl salicylate	IX	35	59	7	2.8	23	7
				62	7	3.2	20	7
				84	6	3.2	19	10
10	Methyl phenyl carbinol	X	41	89	6	3.2	20	12
				90	6	3.2	20	9

A small quantity (3–10 c.c.) of methyl-, ethyl phenyl-acetates, ethyl phenyl-propionate, iso-propyl cinnamate and methyl phenyl carbinol was used for each experiment. From the fact of the coincidence of most of the Raman lines in ethyl phenyl propionate and ethyl cinnamate, it is considered that the small quantity of the cinnamate may be mixed with ethyl phenyl propionate due to the insufficient reduction.

The strong back grounds in the plates of methyl-, ethyl- and phenyl-acetates and methyl- and ethyl salicylates could not be removed even when the pure samples obtained by the repeated purifications were examined. The data of the Raman spectra are tabulated as follows.

Table I.

Methyl phenyl acetate $C_6H_5 \cdot CH_2CO \cdot O \cdot CH_3$.

No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$
1	24440	$^1/_2(b)$	q-2948	26	22169	3(d)	e- 769
2	24293	$^1/_2(b)$	p-3060	27	22120	3(b, d)	e- 818
3	24227	1(b, d)	k- 478	28	22047 ?	0	e- 891
4	24182	0	k- 523	29	22016 ?	0(b)	e- 922
5	24076	$^1/_2(bb)$	k- 629	30	21942	8	e- 996
6	24011	1(b)	k- 694	31	21913	3	e-1025
7	23952	2(b)	k- 753	32	21855	1(d)	e-1083
8	23894	0(b, d)	k- 811	33	21777	3	e-1161(k-2928)
9	23780	1(d)	k- 925	34	21754	5(d)	e-2951(e-1184)
10	23705	5	k-1000	35	21648	7(b, d)	k-3057
11	23681	2	k-1024	36	21562 ?	0	i-2954
12	23593	2(b, d)	k-1112	37	21502	$^1/_2(bb, dd)$	e-1436
13	23542	0(b)	k-1163	38	21338	6(b, d)	e-1600
14	23510	2(b)	k-1195(i-1006)	39	21196 ?	2(bb, dd)	e-1742
15	23434	0(b)	k-1271	40	20016	$^1/_2$	e-2922
16	23399 ?	0(d)	k-1306(i-1117)	41	19984	3(b)	e-2954
17	23311	$^1/_2$	i-1205	42	19881	2	e-3057
18	23274 ?	0	k-1431				
19	23103	2	k-1602				
20	22751	3(d)	e- 187				
21	22576	$^1/_2(b, d)$	e- 362				
22	22455	3(b, d)	e- 483				
23	22408	$^1/^2(d)$	e- 530				
24	22316	3(b)	e- 622				
25	22243	$^1/_2(d)$	e- 695				

$\overline{\Delta\nu}$: 187 (3 d); 362 ($^1/_2$ b, d); 481 (3 b, d); 527 ($^1/_2$ d); 622 (3 b); 695 ($^1/_2$ b, d); 761 (3 d); 818 (3 d); 924 (1 d); 998 (8); 1025 (3); 1083 (1 b); 1112 (3 b, d); 1162 (3 b); (1189) (5 d); (1271) ($^1/_2$ b, d) ?; 1306 ($^1/_2$ b); 1436 ($^1/_2$ bb, dd); 1601 (6 b, d); 1742 (2b, d); 2922 (3 b); 2953 (5 d); 3057 (7 b, d).

Table II.

Ethyl phenyl acetate $C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$.

No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$
1	24404	$^1/_2(d)$	q-2984	21	21969	$^1/_2$	f-1026
2	24302	$^1/_2$	p-3051	22	21944	8	e- 994
3	24238	1(b)	o-3055	23	21913	4	e-1025
4	24084	2(b)	k- 622	24	21823	1(d)	e-1115
5	23957	2	k- 749	25	21775	5(dv)	e-1163(k-2930)
6	23709	5	k- 996	26	21727	5(b, d)	e-1211
7	23683	3	k-1022	27	21623	2(d)	k-2978
8	23604	2(d)	k-1101	28	21650	7(b, d)	k-3055
9	23540	2(d)	k-1165	29	21543	$^1/_2(d)$	e-1395
10	23502	3(d)	k-1203	30	21483	1(bb, dd)	e-1455
11	23443 ?	$^1/_2$	k-1262	31	21338	7(dv)	e-1600
12	23312	$^1/_2$	k-1204	32	21201 ?	$^1/_2(dd)$	e-1737
13	23274	$^1/_2(b, d)$	k-1431	33	20016	2(b)	e-2922
14	23103	1(d)	k-1602	34	19953	2(b)	e-2985
15	22729 ?	$^1/_2(dd)$	e- 209	35	19884	2	e-3054
16	22316	3	e- 622				
17	22258	2(B)	e- 680				
18	22180		e- 758				
19	22150	2(B)	e- 788				
20	22080		e- 858				

$\overline{\Delta\nu}$: 209 ($^1/_2 dd$) ?; 622 (3 b, d); 680 (2 b)—758 (2 b); 788 (2b)—858 (2 b); 997 (8); 1025 (4); 1108 (1 d); 1164 (5 dv); 1207 (5 b, d); (1265) (2 d) ?; 1395 ($^1/_2 d$); 1455 (1 bb, d); 1601 (7 dv); 1737 ($^1/_2 dd$) ?; 2922 (2 b); 2981 (2 b); 3055 (7 b, d).

Table III.

Ethyl phenyl-propionate $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$.

No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$
1	23885	$^1/_2(b)$	k- 820	16	21945	7	e- 993
2	23708	4	k- 997	17	21915	3(d)	e-1023
3	23683	$^1/_2(d)$	k-1023	18	21833	2(d)	e-1105
4	23502	4(b)	k-1203	19	21791	6	k-2914
5	23443	$^1/_2(b, d)$	k-1262	20	21765	6	e-1173
6	23252	$^1/_2(d)$	k-1453	21	21742	6	e-1196
7	23213 ?	$^1/_2(d)$	k-1495	22	21681	6(B)	e-1257(k-3024)
8	23185	2(d)	e+ 247	23	21649		k-3056
9	23111	5	k-1594	24	21495	2(b, d)	e-1443
10	23076	5	k-1629	25	21447	0	e-1491
11	22766	1(d)	e- 178	26	21343	8	e-1595
12	22701	2(dr)	e- 237	27	21310	7	e-1628
13	22599	$^1/_2(d)$	e- 339	28	21277	$^1/_2$	e-1661
14	22320	2(b, d)	e- 618	29	21237	2	e-1701
15	22079	1(b)	e- 859	30	19885	1	e-3053

$\overline{\Delta\nu}$: 178 (1 d); 237 (2 d); 339 ($^1/_2$ d); 618 (2 b, d); (820) ($^1/_2$ b) ?; 859 (1 b); 995 (7); 1023 (2); (1105) (2 d); 1173 (6); 1196 (6); (1257) (5 b) ?; 1379 ($^1/_2$); 1448 (2b, d) ?; 1491 ($^1/_2$); 1595 (8); 1628 (7); 1661 ($^1/_2$); 1701 (2); 2914 (6); 2963 (6) ?; (3024) (5); 3055 (5 b).

Table IV.

Ethyl cinnamate $C_6H_5 \cdot CH{:}CH \cdot CO \cdot O \cdot CH_2\ CH_3$.

No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$
1	24433 ?	0(d)	k- 272	11	23709	6	k- 996
2	24297 ?	0	k- 408	12	23679	1	k-1026
3	24227	0	k- 478(i- 289)	13	23587	1(d, b)	k-1118
4	24119	1(d, b)	i- 397	14	23549	1(d)	i- 967(k-1156)
5	24088	2	k- 617	15	23527	8(d)	k-1178
6	24047	1	i- 469	16	23505	8(d)	k-1200
7	23989	1(bb)	k- 716	17	23446	6(d)	k-1259
8	23869	2	k- 836	18	23400	4	k-1305(i-1110)
9	23839	2(d)	k- 866	19	23375	1	k-1330
10	23729	1(d)	k- 976	20	23342	3(d)	k-1363(i-1174)

Table IV.—(*Concluded*)

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
21	23315	3(*d*)	*k*-1390(*i*-1201)	51	21824	3(*b*, *d*)	*e*-1114
22	23258	5	*k*-1449	52	21782	3(*d*)	*k*-2923
23	23211	5	*k*-1494	53	21760	8(*s*)	*e*-1178
24	23172	2	*k*-1533(*i*-1339)(Hg)	54	21738	8(*s*)	*e*-1200(*k*-2980)
25	23154	1/2	*i*-1362	55	21679	6(*d*)	*e*-1259(*f*-1316)
26	23132	2	*k*-1573(*i*-1384)(Hg)	56	21638	5(*d*)	*e*-1300(*k*-3067)
27	23108	10	*k*-1597	57	21607	3	*e*-1331(*f*-1388)
28	23071	10	*k*-1634	58	21574	3	*e*-1364
29	23020	2	*i*-1496	59	21544	3	*e*-1994
30	22980	2	*i*-1536	60	21491	5	*e*-1447
31	22882	2	*i*-1634	61	21464	1/2	*f*-1531
32	22823	1/2(*b*, *d*)	*f*- 172	62	21445	5	*e*-1493(*i*-3071)
33	22761	2(*b*, *d*)	*e*- 177	63	21400	3	*f*-1595(*e*-1538)
34	22708	1/2(*d*)	*f*- 287(Hg)	64	21367	3	*e*-1571(*f*-1622)
35	22659	1(*b*, *d*)	*e*- 279	65	21341	10	*e*-1597
36	22591	1/2(*d*)	*f*- 404	66	21305	10	*e*-1633
37	22540	2(*d*)	*e*- 398	67	21296	1	*e*-1669
38	22466	0(*d*)	*e*- 472	68	21232	8(*d*)	*e*-1706
39	22367	4	*e*- 571	69	20073	2	*f*-2922
40	22323	6(*s*)	*e*- 615	70	20008	3	*e*-2920(*f*-2987)
41	22221	4(*b*, *d*)	*e*- 717	71	19957	3	*e*-2981
42	22163	3	*e*- 775	72	19874	5(*dv*)	*e*-3064
43	22126	0	*f*- 869				
44	22103	5	*e*- 835				
45	22071	5(*dr*)	*e*- 867				
46	22028	1/2 ?	*f*- 967				
47	21961	1(*d*)	*e*- 977(*f*-1034)				
48	21942	10(*s*)	*e*- 996				
49	21913	3(*s*)	*e*-1025				
50	21778	1/2(*d*)	*f*-1117				

$\overline{\Delta\nu}$: 177 (2 *b*, *d*) ?; 279 (2 *bd*) ?; 403 (2*d*); 475 (0) ?; 571 (4); 616 (6 *s*); 717 (4 *b*, *d*) ?; 836 (5); 867 (5 *d*); 977 (1 *d*); 996 (10 *s*); 1025 (3); 1116 (3 *b*, *d*); (1156) (3); 1178 (8); 1200 (8); 1259 (6 *d*); 1303 (5 *d*); 1331 (3); 1363 (3); 1392 (3); 1447 (5); 1494 (5); (1536) (3); 1572 (3); 1597 (10); 1634 (10); (1669) (1); 1706 (8 *d*); 2922 (3 *d*); 2981 (3); 3067 (5 *d*).

Table V.

Iso-propyl cinnamate $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot CH(CH_3)_2$.

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24093	1/2	*k*- 612	26	21941	8	*e*- 997
2	23897	1/2	*k*- 808	27	21913	1(*d*)	*e*-1025
3	23710	4(*b*)	*k*- 995	28	21883	1(*d*)	*k*-2822
4	23681	1	*k*-1024	29	21825	1	*e*-1113(*k*-2880)
5	23592	1/2(*d*)	*k*-1113	30	21778	1	*k*-2927
6	23526	6(*d*)	*k*-1179	31	21761	7	*e*-1177
7	23505	6	*k*-1200	32	21739	7	*e*-1201
8	23445	4(*b*)	*k*-1260	33	21672	5(*d*)	*e*-1266
9	23401	1/2	*k*-1304(*i*-1115)	34	21632	4(*d*)	*e*-1305
10	23318	1	*k*-1387(*i*-1198)	35	21543	1/2	*e*-1395
11	23254	1	*k*-1451(*i*-1262)	36	21489	4	*e*-1449
12	23209	1	*k*-1496	37	21446	4	*e*-1492(*i*-3070)
13	23107	8	*k*-1598	38	21398	2	*f*-1597
14	23072	8	*k*-1633	39	21367	3	*e*-1571
15	22755	1(*bb*)	*e*- 183	40	21343	9	*e*-1695
16	22399	1/2	*e*- 399	41	21306	10	*e*-1631
17	22463	0	*e*- 475	42	21231	8	*e*-1707
18	22369	1(*d*)	*e*- 569	43	21116	1	*e*-2822
19	22322	4	*e*- 616	44	20016	1(*d*)	*e*-2922
20	22257	1	*e*- 681	45	19962	1/2(*d*)	*e*-2976
21	22211	2	*e*- 727	46	19872	1(*d*)	*e*-3066
22	22168	1	*e*- 770				
23	22122	5	*e*- 816				
24	22077	5	*e*- 861				
25	22047 ?	1/2	*e*- 891				

$\overline{\Delta\nu}$: 183 (1 *bb*); 399 (1/2); 475 (0); 569 (1 *d*); 616 (4); 681 (1); 727 (2); 770 (1); 814 (5); 861 (5); 891 (1/2); 996 (8); 1025 (2); 1113 (1); 1177 (7); 1201 (7); 1266 (5 *d*); 1305 (4 *d*); 1391 (1/2 *d*); 1450 (4); 1494 (4); 1597 (9); 1632 (10); 1707 (8); 2822 (1); 2925 (1 *d*); 2971 (1/2 *d*); 3070 (4 *d*).

Table VI.

Dimethyl phthalate $C_6H_4\cdot(CO\cdot O\cdot CH_3)_2$.

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24435	1/2	q-2953	21	22145	1/2	e- 793
2	24404	1/2	p-2949	22	21974	2(b, d)	e- 964
3	24319	1/2	q-3069(k- 386)	23	21899	6	e-1039
4	23885	2	k- 649	24	21856	1(d)	k-2849
5	23885	3	k- 820	25	21815	3(d)	e-1123
6	23741	1(d)	k- 964	26	21774	1	e-1163
7	23664	5	k-1041	27	21758	4	e-2947
8	23582	1(b, d)	k-1123	28	21666	5(d)	e-1272(i-2850)
9	23548	2(d)	k-1157(i- 968)	29	21633	7(b, d)	k-3072
10	23471	1/2	i-1045	30	21571	0	i-2945
11	23423	4(b, d)	k-1282	31	21492	1	e-1446
12	23265	1/2(d) ?	k-1440	32	21452	1	e-1486
13	23219	1/2	k-1486	33	21360	1/2	e-1578
14	23123	1	k-1582	34	21338	6	e-1600
15	23102	2	k-1603	35	21216	8	e-1722
16	22708	1(d)	e- 230	36	19988	4	e-2950
17	22641	0	e- 297	37	19868	3	e-3070
18	22539	1(d)	e- 399				
19	22287	3(d)	e- 651				
20	22120	6	e- 818				

$\overline{\Delta\nu}$: (230) (1 d) ?; 297 (0); 393 (1 d); 650 (3 d); 793 (1/2); 819 (6); 964 (2 b, d); 1040 (6); 1123 (3 d); 1160 (1); 1277 (5 d); 1443 (1); 1486 (1); 1580 (2); 1602 (6); 1722 (8); 2849 (1 d); 2947 (4); 3071 (7 b, d).

Table VII.

Diethyl phthalate $C_6H_4(CO{\cdot}O{\cdot}CH_2{\cdot}CH_3)_2$.

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24416	1/2	q-2972	26	21836	4(d)	f-1159(k-2869)
2	24319	1(d)	q-3069	27	21816	2(d)	e-1122
3	24058	1(d)	k- 647	28	21779	7(b)	e-1159(k-2926)
4	23925 ?	0 ?	k- 780	29	21731	5(b)	k-2974(f-1264)
5	23860	1(b)	k- 845(i- 656)	30	21670	7(d)	k-1268
6	23670	5	k-1035(i- 846)	31	21632	8(b, d)	k-3073
7	23587	2(b, d)	k-1118	32	21577	2	e-1361(i-2939)
8	23544	2(b, d)	k-1161	33	21536	2	i-2978
9	23432	3(b, d)	k-1273	34	21489	3	e-1449
10	23334	1/2(d)	k-1371	35	21449	2	e-1489(i-3067)
11	23252	2	k-1453(i-1253)	36	21367	2	e-1571
12	23220	1/2	k-1485.	37	21342	9(s)	e-1596
13	23172	0	k-1532	38	21220	8(b)	e-1718
14	23128	3	k-1577	39	20065	1	f-2930(e-2873)
15	23107	5	k-1598	40	20009	2	e-2929
16	22807	4(b, d)	i-1709	41	19965	2	e-2973
17	22592	1(b, d)	e- 346	42	19867	3	e-3071
18	22545	2	e- 393				
19	22294	5(s)	e- 644				
20	22159	2(d)	e- 779(f- 836)				
21	22096	5	e- 842				
22	22015 ?	1/2	e- 923				
23	21982	1/2	f-1013				
24	21922	1	e-1016				
25	21904	8(s)	e-1034				

$\overline{\Delta\nu}$: 346 (1 b, d); 393 (2); 644 (5 s); 779 (2 d); 843 (5); (923) (1/2); 1016 (1); 1034 (8 s); 1120 (2 d); 1160 (2 b); 1270 (7 d); 1362 (2); 1451 (3); 1487 (2); 1530 (1/2) ?; 1574 (3); 1597 (9 s); 1718 (8 b); 2871 (5 d); 2928 (4 b); 2974 (3 b); 3070 (8 b).

Table VIII.

Methyl salicylate $C_6H_4\begin{cases}CO\cdot O\cdot CH_3\\OH\end{cases}$

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24440 ?	1/2	*k*- 265	21	22134	6	*e*- 804
2	24282	1	*k*- 423	22	22093 ?	1/2	*e*- 845
3	24144	4	*k*- 561	23	21907	4	*e*-1031
4	23903	5	*k*- 802	24	21857	1	*e*-1081
5	23866	1/2(*b*)	*k*- 839	25	21808	3(*d*)	*e*-1130
6	23672	4	*k*-1033	26	21754	2	*k*-2951
7	23572	2(*b*, *d*)	*k*-1133	27	21695	5	*e*-1243
8	23460	5	*k*-1245	28	21614	5(*dd*, *b*)	*k*-3091(*e*-1324)
9	23377	5(*b*)	*k*-1328	29	21479	4(*d*)	*e*-1459
10	23270	1/2	*i*-1246	30	21364	1/2	*e*-1574
11	23240	3	*k*-1465	31	21335	1(*d*)	*e*-1603
12	23122	2(*d*)	*k*-1583	32	21266	5(*b*, *d*)	*e*-1672
13	23102 ?	1/2(*d*)	*k*-1603	33	19988	3	*e*-2950
14	22806 ?	1	*f*- 189	34	19861	3(*b*, *d*)	*e*-3077
15	22754	4	*e*- 184				
16	22677	1/2(*d*)	*e*- 261				
17	22582	2	*e*- 356				
18	22515	1	*e*- 423				
19	22424 ?	1/2	*e*- 514				
20	22380	4	*e*- 558				

$\overline{\Delta\nu}$: 184 (4); 264 (1/2 *d*) ?; (356) (2); 423 (1); (514) (1/2) ?; 560 (4); 804 (6); (845) (1/2) ?; 1032 (4); 1081 (1); 1132 (3 *d*); 1244 (5); 1326 (5 *b*, *d*); 1462 (4 *d*); 1578 (2 *d*); 1603 (1 *d*); 1672 (5 *b*, *d*); 2950 (3); 3084 (5 *bb*, *dd*).

Table IX.

Ethyl salicylate $C_6H_4\begin{cases}CO\cdot O\cdot CH_2\cdot CH_3\\OH\end{cases}$

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24402	1/2	*q*-2986	21	21901	4	*e*-1037
2	24253	2	*k*- 453	22	21830	1	*k*-2875
3	24143	4	*k*- 562	23	21773	1(*b*)	*k*-2932
4	23898	4	*k*- 807	24	21727	1	*k*-2978
5	23856	3	*k*- 849	25	21696	6(*b*)	*e*-1242
6	23674	4	*k*-1031	26	21621	5(*b*, *d*)	*k*-3084(*e*-1031)
7	23364	1/2(*d*) ?	*k*-1141	27	21575	1/2	*e*-1363
8	23462	5(*b*)	*k*-1243	28	21540	1/2	*e*-1398
9	23387	5(*b*)	*k*-1318	29	21479	4(*d*)	*e*-1459
10	23339	1/2 ?	*k*-1366	30	21327	1/2(*b*, *d*)?	*f*-1668
11	23312	1/2 ?	*k*-1393	31	21268	5(*d*)	*e*-1670
12	23238	4(*b*, *d*)	*k*-1467	32	20065	1(*d*)	*e*-2873
13	23119	1(*b*, *d*)	*i*-1396(*k*-1586)	33	20007	1(*d*)	*e*-2931(*f*-9288)
14	23102	1(*b*, *d*)	*k*-1603	34	19954	1(*d*)	*e*-2984
15	22771	3(*b*, *d*)	*e*- 167	35	19861	3(*b*, *d*)	*e*-3077
16	22693	2(*d*) ?	*e*- 245				
17	22481	1/2(*d*)	*e*- 457				
18	22381	4	*e*- 557				
19	22129	3	*e*- 809				
20	22090	2	*e*- 848				

$\bar{\Delta\nu}$: 167 (3 *b*, *d*); 245 (1/2 *d*) ?; 452 (2) ?; 559 (4); 808 (4); 848 (2); 1034 (4); 1141 (1/2 *b*); 1242 (6); 1318 (5 *b*, *d*); 1366 (1/2); 1395 (1/2); 1463 (4 *b*, *d*); (1586) (1 *b*, *d*) ?; 1605 (1/2 *b*, *d*) ?; 1670 (5 *d*); 2932 (1 *d*); 2980 (1 *d*); 3080 (5 *b*, *d*).

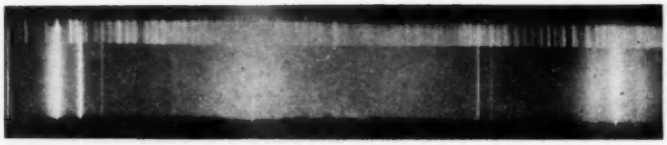
Table X.

Methyl phenyl carbinol $C_6H_5 \cdot \underset{\underset{OH}{|}}{CH} - CH_3$.

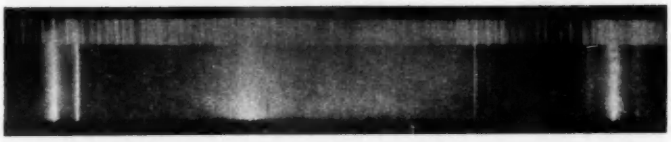
No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$
1	24219	1/2	*k*- 786	26	21865	1/2(*b*, *d*)	*e*-1073
2	23943	1/2(*d*)	*k*- 762	27	21835	1/2(*d*)	*e*-1103
3	23902	1/2(*d*)	*i*- 614	28	21783	5(*dr*)	*k*-2922(*f*-1212)
4	23711	5	*k*- 994	29	21740	7	*e*-1198(*k*-2965)
5	23684	2	*k*-1021	30	21674	1	*e*-1264
6	23500	1/2(*d*)	*k*-1205(*i*-1016)	31	21651	8(*b*, *d*)	*k*-3054
7	24437	1/2(*d*)	*k*-1268	32	21596	0(*d*)	*i*-2920
8	24311	0	*k*-1394(*i*-1205)	33	21543	1	*e*-1395(*i*-2973)
9	23257	1/2	*k*-1448	34	21494	2(*d*)	*e*-1444
10	23189	2(*d*)	*k*-1516(*e*- 251)	35	21458	3	*i*-3058
11	23108	5(*d*)	*k*-1597	36	21341	8	*e*-1597
12	22797	5(*b*, *d*)	*e*- 141	37	21261	4(*b*, *d*)	*e*-1678
13	22689	2(*b*, *d*)	*e*- 249	38	20081	1	*f*-2914
14	22619	1(*d*)	*e*- 319(*f*- 376)	39	20019	2	*e*-2919
15	22561	0(*b*, *d*)	*e*- 377	40	19964	1/2(*d*)	*e*-2974
16	22458	1/2(*d*)	*e*- 480(*f*- 531)	41	19886	5(*b*)	*e*-3052
17	22407	1/2	*e*- 531				
18	22324	4	*e*- 614				
19	22216	1/2	*f*- 779 ?				
20	22174	4(*b*)	*e*- 764				
21	22086	1/2(*d*)	*e*- 852 ?				
22	22039	2(*b*)	*e*- 899				
23	21980 ?	0	*f*-1015				
24	21947	10	*e*- 991				
25	21918	5	*e*-1020				

$\overline{\Delta\nu}$: 141 (5 *b*, *d*); 249 (2 *b*, *d*); (319) (1 *d*) ?; (377) (0 *d*) ?; 483 (1/2); (531) (1/2) ?; 614 (4); 763 (4 *b*); 852 (1/2 *d*); 899 (2 *b*); 993 (10); 1021 (1/2); 1073 (1/2 *b*, *d*); (1103) (1/2 *d*); (1161) (5 *d*) ?; 1201 (7); 1395 (1); 1446 (2 *d*); 1597 (8); 1678 (4 *b*, *d*); 2922 (5 *dr*); 2971 (7) ?; 3054 (8 *b*, *d*).

(1) Methyl phenyl acetate $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CH_3$

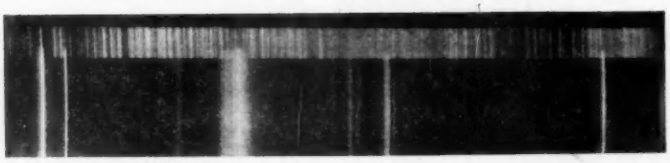


(2) Ethyl phenyl acetate $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CH_2CH_3$



(3) Ethyl phenyl propionate $C_6H_5{\cdot}CH_2CH_2{\cdot}CO{\cdot}O{\cdot}CH_2CH_3$

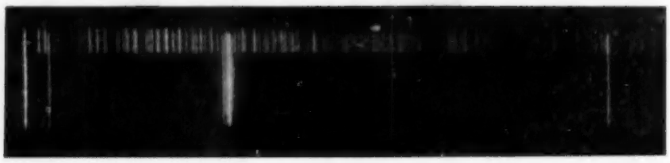
(4) Ethyl cinnamate $C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}O{\cdot}CH_2CH_3$



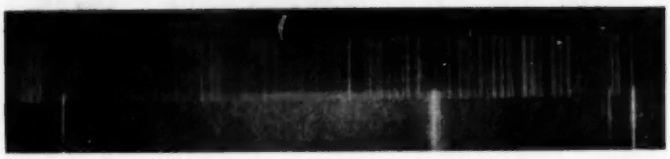
(5) Iso-propyl cinnamate $C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}O{\cdot}CH(CH_3)_2$

(6) Di-methyl phthalate $C_6H_4\cdot(CO\cdot O\cdot CH_3)_2$

(7) Di-ethyl phthalate $C_6H_4\cdot(CO\cdot O\cdot CH_2CH_3)_2$



(8) Methyl salicylate $C_6H_4\begin{cases}CO\cdot O\cdot CH_3\\OH\end{cases}$



(9) Ethyl salicylate $C_6H_4\begin{cases}CO\cdot O\cdot CH_2CH_3\\OH\end{cases}$

(10) Methyl phenyl carbinol $C_6H_5\cdot CH\begin{cases}CH_3\\OH\end{cases}$

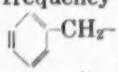
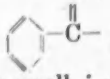
Discussion of the Results. As reported in this and the previous paper,[1] the frequency of $\Delta\nu = 3060$ cm.$^{-1}$ which has been known to be attributable to the C—H linkage in the benzene ring, was found as one of the most intense lines in the Raman spectra of the aromatic compounds investigated. For the comparison, the data observed are shown in the following :

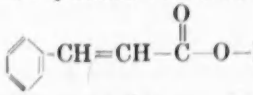
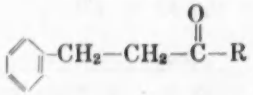
$C_6H_5\cdot CO\cdot O\cdot R$	3070 cm.$^{-1}$	$C_6H_5\cdot CO\cdot Cl$	3067 cm.$^{-1}$
$C_6H_5\cdot CH_2\cdot CO\cdot O\cdot R$	3057	$C_6H_5\cdot O\cdot CO\cdot R$	3062
$C_6H_5\cdot CH_2\cdot CH_2\cdot CO\cdot O\cdot R$	3056	$CH_3\cdot C_6H_4\cdot O\cdot CO\cdot R$	3053
$C_6H_5\cdot CH{:}CH\cdot CO\cdot O\cdot R$	3067	$HO\cdot C_6H_4\cdot CO\cdot O\cdot R$	3080
$C_6H_5\cdot \underset{(OH)}{CH}\text{–}CH_3$	3054	$C_6H_4\cdot(CO\cdot O\cdot R)_2$	3070

The results of other authors[2] are ;

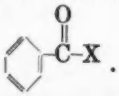
$C_6H_5\cdot CH_3$	3054 cm.$^{-1}$	$C_6H_5\cdot CH_2NO_2$	3059 cm.$^{-1}$
$C_6H_5\cdot CH_2\cdot Cl$	3054	$C_6H_5\cdot CH_2\cdot CH{:}CH_2$	3057
$C_6H_5\cdot CH_2\cdot NH_2$	3050	$C_6H_5\cdot CH_2\cdot CBr{:}CH_2$	3056
$C_6H_5\cdot CH_2\cdot OH$	3050	$C_6H_5\cdot CO\cdot C_6H_5$	3052
$C_6H_5\cdot CH_2\cdot CN$	3057		

From these experimental data, we may suppose that in the aromatic compounds this frequency is influenced, to the first degree of approximation, only by the characteristics of the group or the atom adjacent to the carbon atom in the benzene ring.

It is observed that the frequency in question is found to be $\Delta\nu = 3055$ cm.$^{-1}$ in the compounds of  type, 3065 cm.$^{-1}$ in those of type and 3070 cm.$^{-1}$ in those of  type. In the case of $C_6H_5\cdot CO\cdot C_6H_5$[3] the shift is exceptionally small, i.e. is 3052 cm.$^{-1}$ which may be due to its symmetric form.

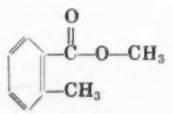
The fact that the frequency in question is found to be 3067 cm.$^{-1}$ in ethyl and iso-propyl cinnamates  and 3056 cm.$^{-1}$ in ethyl phenyl propionate  shows that the higher

(9) Kohlrausch, " Der Smekal-Raman Effect," 328–332.

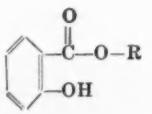
value of the frequency is due to the influence of the double bond of the carbon, $-\overset{\|}{C}-$, adjacent to the benzene ring, viz.,  .

Systematic studies[10] of the derivatives of benzene have shown that the benzene nucleus is characterized by a number of very constant frequencies, viz., $\Delta\nu = 616$, 1000, 1166 and 1595 cm.$^{-1}$, and the aromatic C—H frequency of 3060 cm.$^{-1}$ which has been just mentioned.

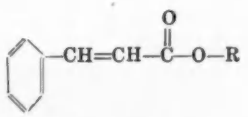
In the present experiment, it was observed that frequencies of $\Delta\nu = 615$ and 1000 cm.$^{-1}$ were shown in a good constancy in monoderivatives of benzene and they disappeared in the case of di-derivatives such as phthalates, salicylates and *o*-kresyl acetates. In place of 615 cm.$^{-1}$ in the di-derivatives (ortho), however, the frequency of $\Delta\nu = 562$ cm.$^{-1}$ in *o*-kresyl-acetate and 560 cm.$^{-1}$ in methyl and ethyl salicylate were observed with the same intensity. And both the frequencies of $\Delta\nu = 571$ and 616 cm.$^{-1}$ were observed in ethyl and iso-propyl cinnamates.



$\Delta\nu = 562$ cm.$^{-1}$



$\Delta\nu = 560$ cm.$^{-1}$



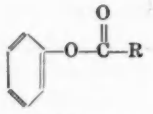
$\Delta\nu = 571$, 616 cm.$^{-1}$

Since all the substances studied contain the C=O group, the comparison of the influences on the frequency due to this linkage seems to be interesting. The lines associated with this linkage are broad, diffuse and intense. The constitutive influences of the substituents attached to the carbonyl group have been studied by Dadieu-Kohlrausch.[11] Considering the data we obtained in the previous and the present experiments the following facts are recognized.

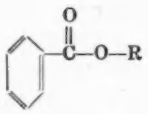
The C:O frequency is directly influenced by an atom or atom group attached directly to it, and independent of the group faraway from it. As shown below, in the cases of phenol esters of fatty acids and *o*-kresyl acetate, the shifts due to the C:O group are practically the same, i.e., 1760 and 1764 cm.$^{-1}$ So are the cases in the benzoates and the alkyl phthalates, the value of the shift in the latter esters decreases about 40 cm.$^{-1}$ from that of the former.

(10) *Monat. Chem.*, **60** (1932), 253; **61** (1932), 426; Kohlrausch, "Smekal-Raman Effect," 227.

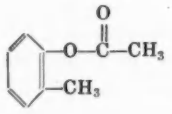
(11) *Ber.*, (B) **66** (1933), 1-12; Kohlrausch, "Smekal-Raman Effect," 157.



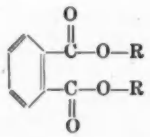
$\Delta\nu = 1761$ cm.$^{-1}$



$\Delta\nu = 1720$.

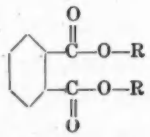


$\Delta\nu = 1764$ cm.$^{-1}$

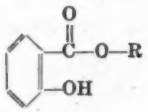


$\Delta\nu = 1718$ cm.$^{-1}$

In the case of salicylates, the OH group exerts a remarkable influence on the C:O linkage, even when the OH group is not directly attached to the same carbon atom of the C:O linkage. By the exchange of the –CO—O—R group of alkyl phthalates into OH, the shift decreases from 1718 cm.$^{-1}$ to 1672 cm.$^{-1}$

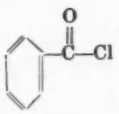


$\Delta\nu = 1718$ cm.$^{-1}$

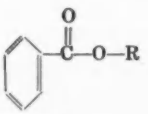


$\Delta\nu = 1672$ cm.$^{-1}$

On the other hand, the Cl atom seems to exert an opposite influence on the C:O group. Benzoyl chloride[1] and acetyl chloride[12] have the high values of 1768 and 1797 cm.$^{-1}$ respectively, compared with the low values of alkyl benzoates and acetyl acetate.



$\Delta\nu = 1768$ cm.$^{-1}$



$\Delta\nu = 1720$ cm.$^{-1}$

$CH_3 \cdot CO \cdot Cl$

$\Delta\nu = 1797$ cm.$^{-1}$

$CH_3 \cdot CO \cdot O \cdot CH_3$

$\Delta\nu = 1737$ cm.$^{-1}$

(12) Kohlrausch, "Smekal-Raman Effect," 318.

Thus the difference between the frequencies of C=O linkage in esters and the corresponding acid chlorides is about 50 cm.$^{-1}$

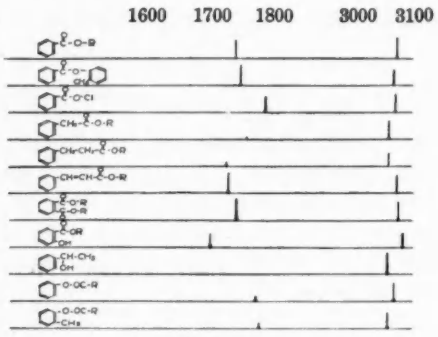


Fig. 1.

It was observed that the intensities of the frequencies due to the C=O linkage are strong in the case of esters of benzoic acid, cinnamic acid, phthalic acid, salicylic acid and benzoyl chloride, but weak in the case of phenol esters of fatty acids, alkyl esters of phenylacetic acid and ethyl ester of phenyl propionic acid. The difference of the intensities of these two kinds is so distinct that we can recognize it even under the visual measurement. It may be considered, in this case, that the –C=C– attached to the –C=O group strengthens the intensity of the latter linkage.

The frequency of $\Delta\nu$=804 in methyl salicylate and that of 814 cm.$^{-1}$ in dimethyl phthalate seems to be corresponded to that of 814 cm.$^{-1}$ in methyl benzoate[1] which may be attributable to the frequency of the system of $-C(=O)-O-CH_3$. In ethyl salicylate and diethyl phthalate, the frequencies of 845 and 843 cm.$^{-1}$ have been observed, which may be attributable to the vibration of the system $-C(=O)-O-CH_2-$ as in the case of ethyl benzoate.[1] A very weak line of $\Delta\nu$ = 845 in methyl salicylate observed may be considered as due to its impurity. These two kinds of frequencies were observed also in methyl- and ethyl-phenylacetates. They were, however, broad and

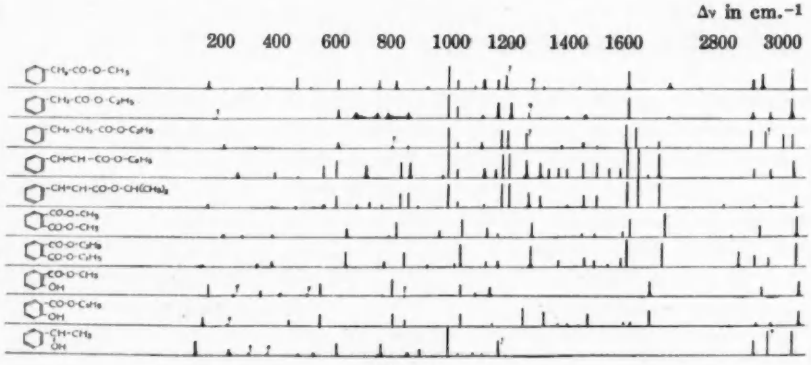
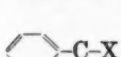
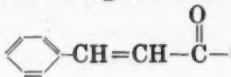
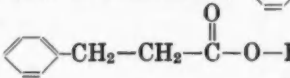
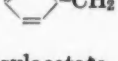
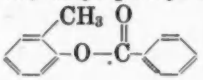
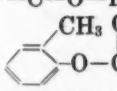


Fig. 2.

diffuse, moreover, on acount of the strong back ground appeared on the plates, the measurement could not be done exactly.

Two frequencies of 836, 867 cm.$^{-1}$ in ethyl cinnamate and 814, 867 cm.$^{-1}$ in iso-propyl cinnamate were clearly observed. It may be explained that the lower frequencies, viz., 836 in ethyl- and 814 cm.$^{-1}$ in iso-propyl cinnamates, are arising from the same origin mentioned above, namely that they are caused by the $-\overset{\|}{C}\overset{O}{\diagup}\diagdown CH_2-$ or $-\overset{\|}{C}\overset{O}{\diagup}\diagdown CH_3$ group, but the higher one, viz., 867 in both cases is caused by other linkage of the molecular rest. The confirmation on the facts however, will be made in near future, by studying the corresponding acid and other compounds.

The frequency of 763 cm.$^{-1}$ in methyl phenyl carbinol is estimated as the vibration between benzene ring and the carbon atom attached to it. The reason is this. The same frequency is observed in all the substances which have a vibration system, benzene ring and an attaching carbon like;  , such as cinnamates,  , ethyl phenyl propionate,  , alkyl phenyl acetates,  ,  , *o*-kresyl benzoate, , *o*-kresylacetate,  , as shown in these experiments. Toluol, ethyl benzol and phenyl nitromethane[13] etc. have also the same shift in their Raman spectra.

Summary.

(1) The Raman spectra of methyl phenylacetate, ethyl phenylacetate, ethyl phenylpropionate, ethyl cinnamate, iso-propyl cinnamate, dimethyl phthalate, diethyl phthalate, methyl salicylate, ethyl salicylate and methyl phenyl carbinol were studied.

(2) The constitutive influences exerted on the C—H of the benzene ring were observed. It was found that the carbon with the double bond $(-\overset{\|}{C}-)$ attached to the benzene ring $(\langle\rangle-\overset{\|}{C}-)$, such as in the case of $C_6H_5\cdot CO\cdot O\cdot R$ and $C_6H_5\cdot CH=CH\cdot CO\cdot O\cdot R$ gave the higher frequency ($\Delta\nu$ = 3070) than that ($\Delta\nu$ = 3055) in the case of $C_6H_5\cdot CH_2\cdot\overset{\|}{C}(O)-O-R$ and other

(13) Kohlrausch, "Smekal-Raman Effect," 329–332.

compounds of the type, $C_6H_5 \cdot CH_2 - X$ which have no carbon with double bond directly attached to the benzene ring.

(3) The constitutive influences exerted on the carbonyl group were observed.

(4) Disappearance of 615 cm.$^{-1}$ in diderivatives and appearance of 560 cm.$^{-1}$ in salicylates, *o*-kresyl acetate, *o*-kresyl benzoate and cinnamate were observed.

(5) Estimation of the valency frequencies of the $-\overset{\|}{C}\overset{O}{\diagup\diagdown}CH_2-$ linkage was confirmed.

Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku.

CORRECTION.

Correction to the previous paper on "Studies of the Raman effect of organic substances (Part I)," in Volume 8.

Page	Line	For	Read
355	12	The fact that carbon dioxide[19] reveals a system of valency frequencies at 2295, 1285, 1223 and 673 leads us	The fact that carbon dioxide[19] has a system of fundamental frequencies at 2295, (1285), 1223 and 673 leads us .....